CARBENE-CARBENE REARRANGEMENTS: EVIDENCE FOR A CYCLOPROPENE INTERMEDIATE

By

THOMAS TYLER COBURN

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

CARBENE-CARBENE REARRANGEMENTS: EVIDENCE FOR A CYCLOPROPENE INTERMEDIATE

By

Thomas Tyler Coburn

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Chairman: William M. Jones
Major Department: Chemistry

Evidence is presented that implicates a fused cyclopropene intermediate in the interconversion of aromatic carbenes and arylcarbenes. A carbene potentially capable of rearrangement with the requisite fused cyclopropene intermediate incorporated into an annelated bicyclo[3.1.0]hex-6-ene structure (acenaphthylcarbene) is sufficiently strained to avoid rearrangement in solution, although gas phase isomerization (410°) still occurs. When the required rearrangement intermediate has an annelated bicyclo[4.1.0]-hept-7-ene structure (dibenzo[*a*,*c*]cycloheptatrienylidene), rearrangement takes place readily in solution at room temperature and below. Annelated cycloheptatrienylidenes in which the loss in resonance energy accompanying cyclopropene forma-

tion is minimized to the greatest extent are most susceptible to reorganization. In the case of unsymmetrical carbenes, the direction of rearrangement is controlled by the relative stabilities of the two potential cyclopropene intermediates.

A convenient, high yield synthesis of 5*H*-dibenzo-[*a*,*c*]cyclohepten-5-one is developed, and the properties of dibenzo[*a*,*c*]cycloheptatrienylidene are examined. Dibenzo-[*a*,*c*]cycloheptatrienylidene and 4,5-benzocycloheptatrienylidene rearrange rapidly in solution, and when the rearrangements take place in the presence of dienes, Diels-Alder adducts of the cyclopropene intermediates are obtained. The structure of these adducts can be deduced from a comparison of their ^{1}H-nmr spectral properties with those of model compounds previously characterized. The molecular geometry of the single furan adduct of dibenzo[*a*,*c*]cycloheptatrienylidene is determined from an analysis of lanthanide-induce proton nmr shifts. Both carbenes react with cyclopentadiene to yield only the *endo-anti* isomer expected to result from cycloaddition of 3-monosubstituted cyclopropenes with this diene.

Furan adducts are obtained under both thermal (125°) and photochemical (30° and -60°) conditions. Tetracyclone adducts result from thermal generation of the carbenes, and cyclopentadiene and butadiene adducts are obtained from low temperature (-60°) reactions of the cyclopropene intermediate which forms from the photolytically generated carbene. The adducts are shown not to be secondary photo-products, and a two step thermal process is ruled out. Also, irreversible

cyclopropene formation competitive with rearrangement is shown to be an unsatisfactory explanation of the experimental results.

Cycloheptatrienylidene, which has been previously shown not to rearrange in solution, reacts with dienes to give adducts that apparently result from a two step process. The thermal reaction of cycloheptatrienylidene with tetracyclone offers no conclusive evidence that cyclopropene trapping occurs. Although the furan-cycloheptatrienylidene adduct has the correct gross structure for formation by cyclopropene trapping, an *endo* transition state would be demanded. Since dibenzo[*a*,*c*]cycloheptatrienylidene reacts with furan via an *exo* transition state and since steric and secondary orbital effects fail to indicate any reason for the differing modes of cycloaddition, a two step mechanism for the cycloheptatrienylidene reaction is suggested.

Phenanthrylcarbene, which does not ring expand in solution, fails to give any indication of cyclopropene formation when generated in solutions containing dienes. Phenylnitrene also fails to react with furan although it is known to rearrange in solution. Although there is no assurance that this diene is adequate for 2*H*-azirine trapping, the possibility that nitrenes rearrange via a Wolff-type mechanism rather than through 2*H*-azirine intermediates is discussed. The information these cyclopropene trapping experiments provide in understanding the mechanism of carbene-carbene rearrangements and the generality of these conclusions is analyzed.

INTRODUCTION

Unlike other reactive intermediates which are highly susceptible to rearrangement, carbenes generally undergo intra- or intermolecular abstraction, insertion, or addition reactions rather than conversion to isomeric carbenes of greater stability. The rearrangement of aromatic carbenes to arylcarbenes (and the reverse reaction) is a notable exception to this generality. Besides detailed studies concerned with the conversion of phenylcarbene (1) and its derivatives to cycloheptatrienylidenes (2) in the gas phase[1] and of benzocycloheptatrienylidene (3) to naphthylcarbene (4) in solution,[1,2] a growing number of heterocyclic[3,4] and nonbenzenoid[5] carbenes have been shown to undergo isomerization. Yet the mechanism of this reorganization remains a subject of considerable conjecture. Some suggested mechanistic alternatives are collected in Figure 1.

A cyclopropene intermediate (5) (Figure 1a) has been widely assumed.[1-10] This mode of rearrangement is suggested by the well known synthesis of cyclopropenes from vinylcarbenes.[11] However, the strain in such a bicyclic structure may be sufficient to prevent its intermediacy, making a concerted rearrangement via a cyclopropene-like transition state (Figure 1b) a reasonable alternative.[2,10] Also, isomerization of an aromatic carbene to the cyclopropene 5 may be

Mechanisms of Rearrangement

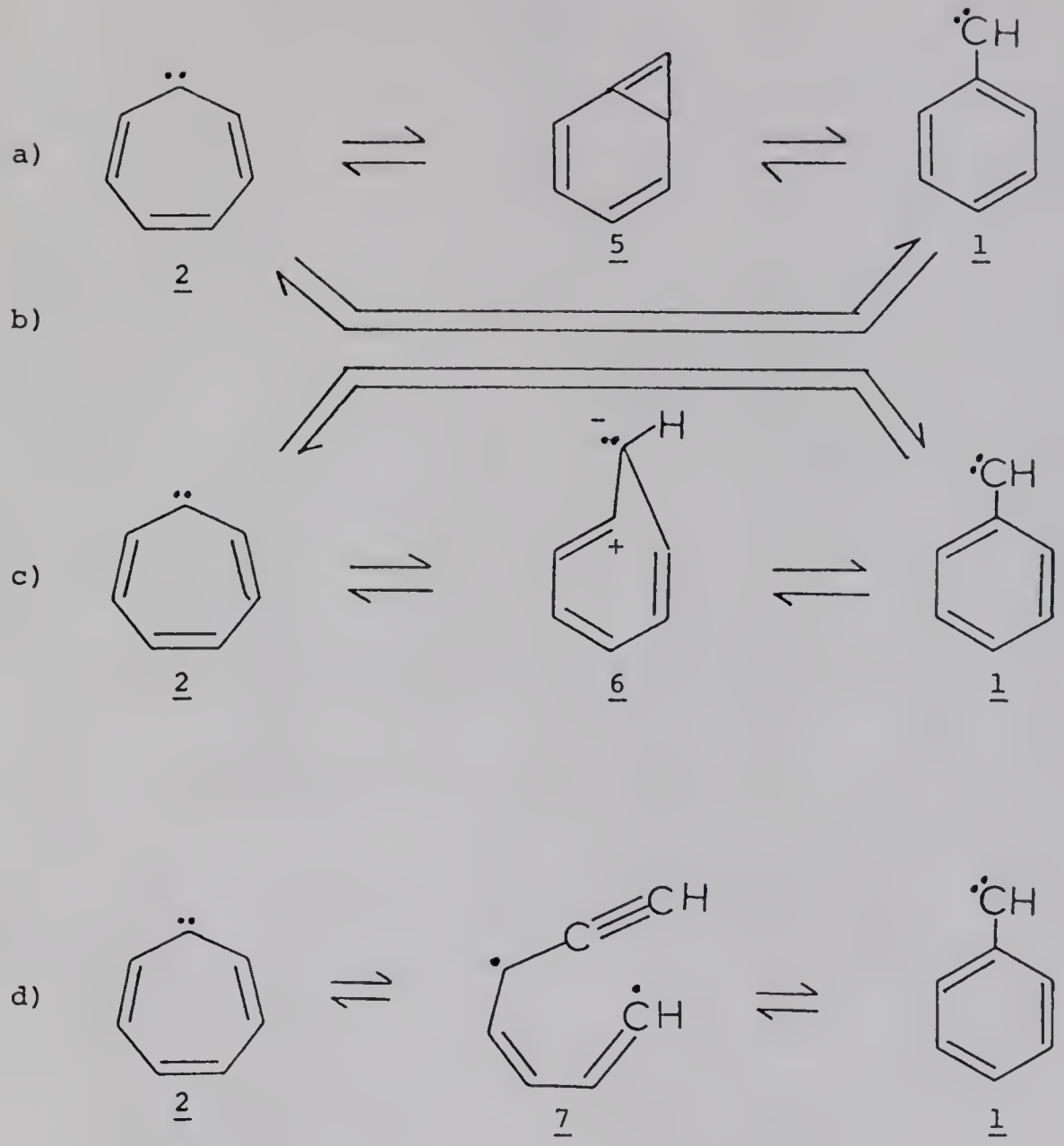
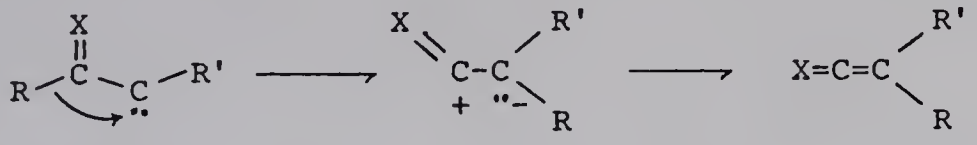


Figure 1

vitiated by the conformational restrictions placed on the carbene center. Such restrictions may be sufficient to preclude the required favorable interaction of carbene orbitals with the double bond.

A mechanism based on that of the Wolff Rearrangement--actually a "retro-Wolff" mechanism for aromatic carbene to arylcarbene isomerization (Figure 1c)-- has also been suggested.[1,2,4,10] Products result from migration of a single



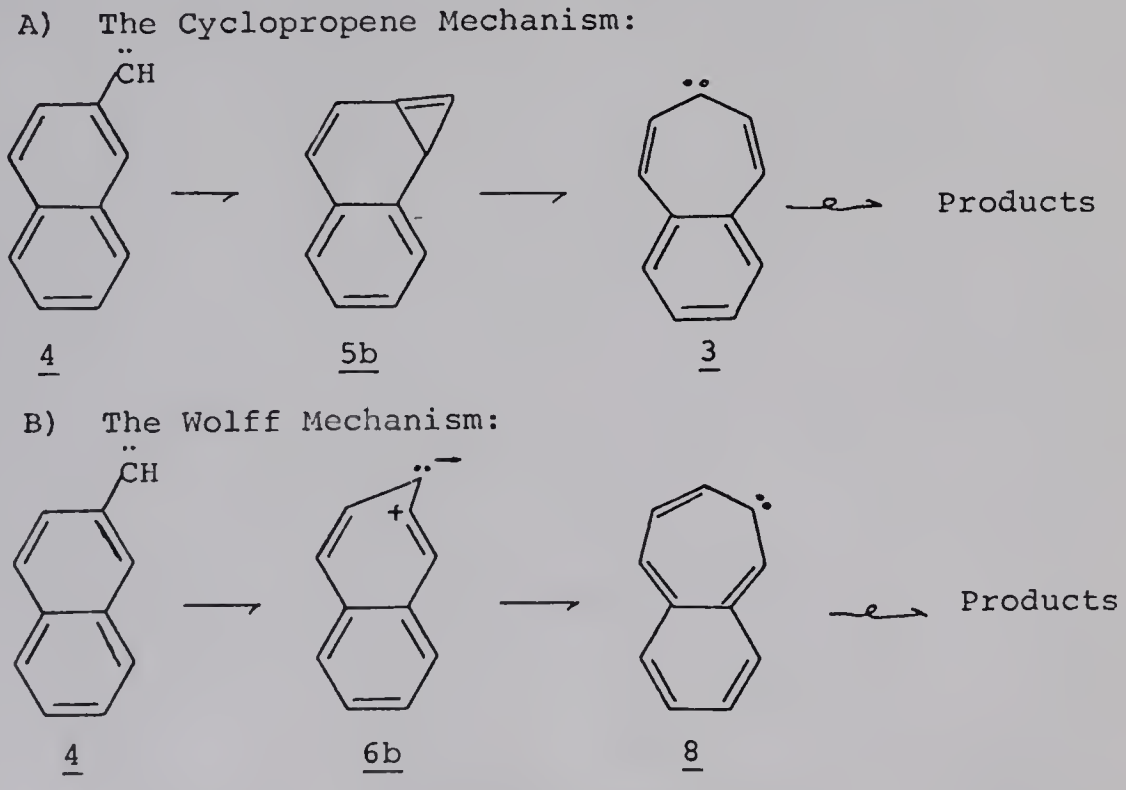
bonded α-substituent to the carbene center. This mechanism when applied to the isomerization of arylcarbenes requires a highly strained, cyclic, bent vinyl cation (6), as a distinct intermediate, or, as preferred by some workers,[4] as a transient stage along a concerted reaction profile. The strain in this charge separated structure may be qualitatively similar to that in a cyclopropene intermediate or transition state, but 6 has one less σ-bond than 5.

Ring opened diradicals (7) (or charge separated species) such as those postulated in nitrene rearrangements[12] have also been suggested (Figure 1d).[1,10] The low temperature employed for some rearrangements,[1,2,5] the absence of hydrogen abstraction products or other products from a radical precursor when the rearrangement occurs in ether solvents,[1,2] and the dramatic acceleration of the reorganization on annelation,[1,2] make a ring opening mechanism unattractive.

Other mechanistic proposals can be ruled out on similar grounds and, in fact, appear even less likely. For example, isomerization of the aromatic carbene to the 7-norcaradienylidene followed by a rearrangement such as that suggested by Skattabøl for the vinylcyclopropylidene to cyclopentenylidene reorganization[13] appears quite unlikely.[1] Strict adherence to Skattabøl's process requires 7-norbornadienylidene as an intermediate that isomerizes cleanly to the arylcarbene leaving no evidence of its presence (even under conditions where products from both aromatic and arylcarbenes are detected[1]). There is no precedent for this highly specific rearrangement of 7-norbornadienylidene to phenylcarbene (1), and to avoid the necessity of this carbene an unusual multiple bond fission of the tricyclopentane intermediate must occur. The multiple bond forming reaction necessary for the reverse reaction requires a startling coincidence of orbital interaction that boggles the imagination. Therefore, this mechanistic possibility seems unworthy of detailed consideration. Other examples of "unlikely" mechanisms include those postulated for the isomerization of arylcarbenes.[6,9] A number of these mechanisms have been previously eliminated with labeling experiments, but such mechanisms are largely inapplicable to the present discussion anyway since they avoid the intermediacy of an aromatic carbene.

Indirect evidence that favors a cyclopropene intermediate or transition state has been previously presented.[1,2,10]

The cyclopropene mechanism (Figure 1a) differs from the Wolff mechanism (Figure 1c) in the extent of double bond character in the reacting bond. An experimental test of bond order versus degree of bond migration employing naphthylcarbenes showed exclusive migration of the bond of higher order just as expected for a rearrangement proceeding via cyclopropene (5b) formation (Figure 2a). The mild experimental conditions which permit contraction of benzocycloheptatrienylidene (3) to naphthylcarbene (4) when compared with those required for the phenylcarbene (1) to cycloheptatrienylidene (2) reorganization argues against an intermediate in which the aromaticity of the additional aromatic ring is reduced [as occurs if the bond of lower order migrates by a Wolff mechanism (Figure 2b)].



Isomerization of β-Naphthylcarbene

Figure 2

Wentrup, Mayor, and Gleiter have recently criticized the suitability of this indirect evidence as grounds for dismissing the Wolff mechanism.[4] They point out that the bond of higher order may migrate by a Wolff mechanism in order to avoid the high energy β-benzocycloheptatrienylidene intermediate 8 that results from migration of the bond of lower order. Examples of nitrene-carbene isomerizations[14] and heterocyclic carbene rearrangements[4] are offered to support the contention that "ring expansions in aromatic carbenes are largely determined by the energy differences between the first reacting species and the product."[14] The mechanistic differences between nitrene-carbene rearrangements and carbene-carbene rearrangements are more stricking than the similarities. Thus, it is doubtful that mechanistic conclusions extracted from analysis of nitrene isomerizations can necessarily be extended to carbon analogues. Nevertheless, the need for more direct evidence pertaining to the mechanistic question is clear.

CHAPTER I

A Norcaradiene-Bisnorcaradiene

Of those intermediates postulated, the cyclopropene 5 seems most easily demonstrated if present since reactions and properties of cyclopropenes are well understood,[15] while those of other potential intermediates are much more speculative. Also, indirect evidence makes a cyclopropene 5 appear to be the most likely intermediate[1,10] so it seems advisable to devise experiments aimed at detecting 5.

The report by Mitsuhashi and Jones[16] that cycloheptatrienylidene (2) reacts with 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) to yield two 7*H*-benzocycloheptenes, 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) is surprising since Dürr and coworkers report[17,18] generation of the same proposed intermediates, 1,2,3,4-tetraphenyl-1a*H*-benzocycloheptene (11) or its norcaradiene-bisnorcaradiene isomer (12), from tetraphenylcyclopentadienylidene in benzene and obtain a single product, 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9). If these reports are correct, an additional intermediate must be involved in the cycloheptatrienylidene reaction that is inaccessible via the cyclopentadienylidene route. A possible explanation is outlined in Figure 3. It requires that the cycloheptatriene to norcaradiene-bisnorcaradiene isomerization in this system be inopperative due to the much

more rapid occurance of a [1.5]-hydrogen shift. Although such an hypothesis (norcaradiene isomerization having a higher activation energy[19] than a [1.5]-shift[20]) is unprecedented, rapid cycloheptatriene--norcaradiene equilibration

A Mechanistic Hypothesis

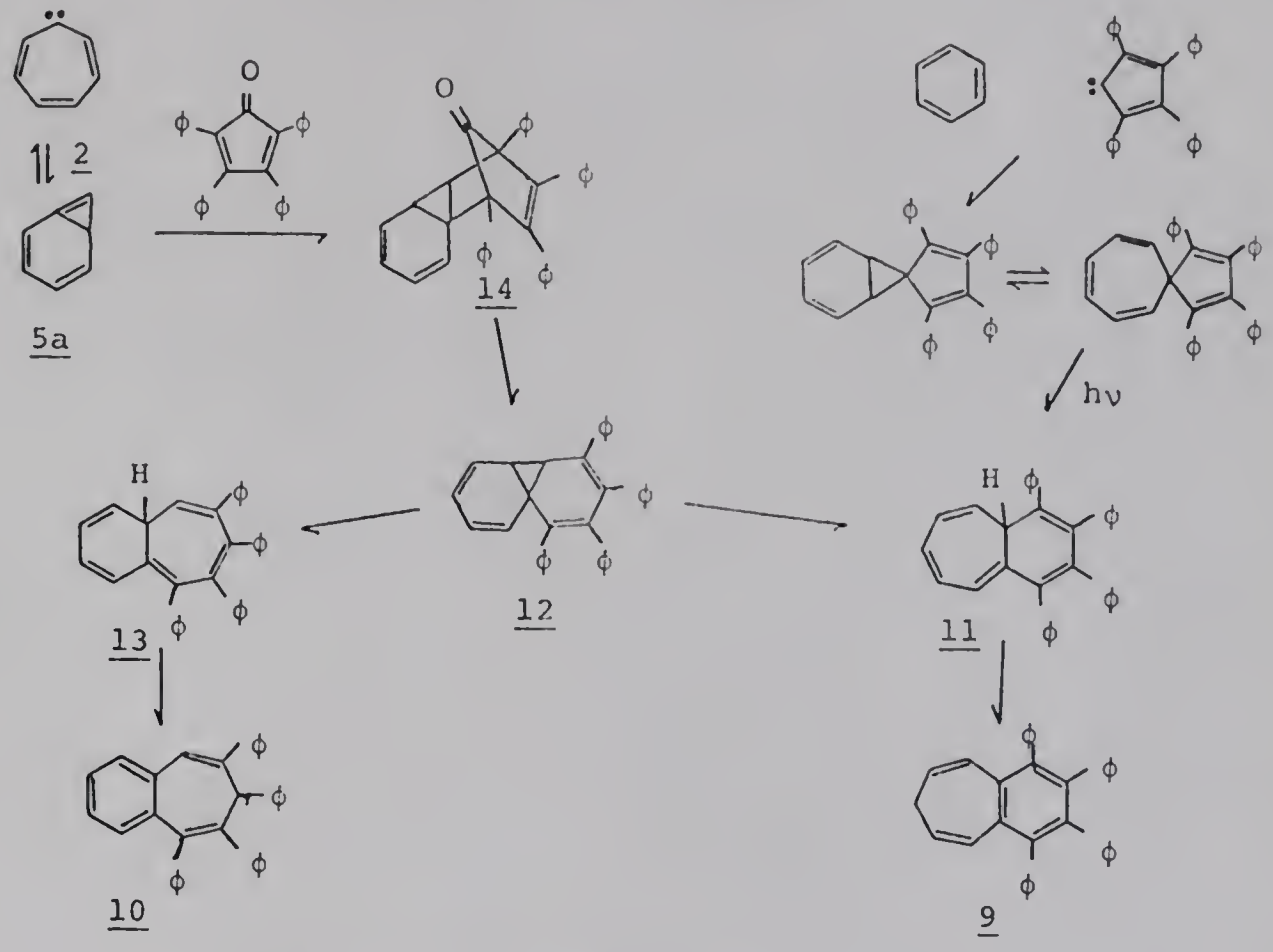
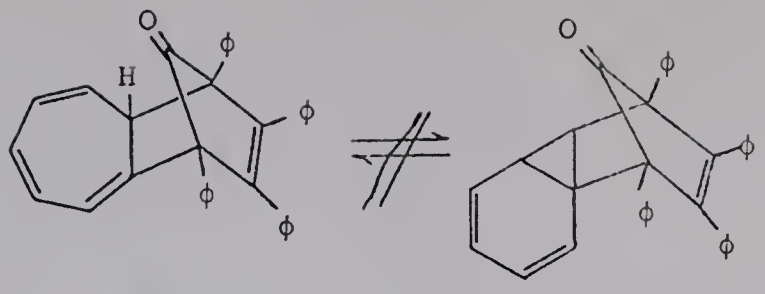


Figure 3

would demand identical products and product ratios regardless of the mode of entry into the equilibrating system. If the cycloheptatriene to norcaradiene isomerization is prevented by incorporation of the potential norcaradiene into a norcaradiene-bisnorcaradiene skeleton, the direct cycloheptatrienylidene adduct to tetracyclone 15 should fail to isomerize to 14 as well. Independent preparation of 15,



15 14

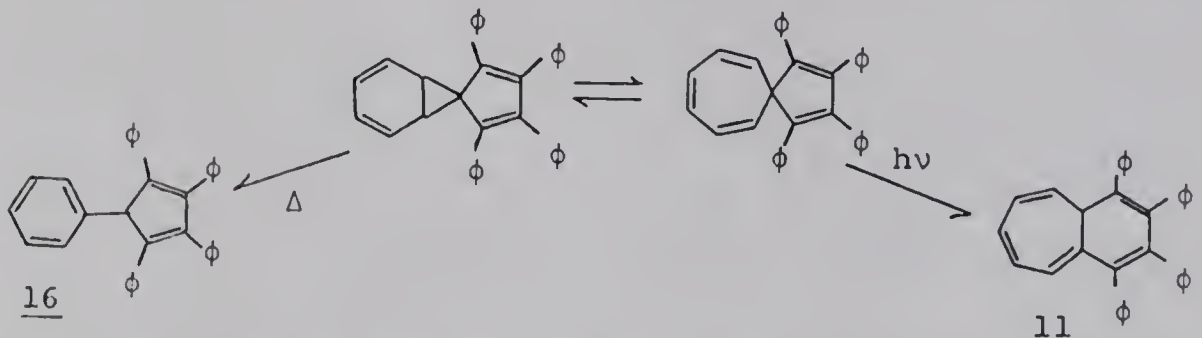
subjection of 15 to the reaction conditions, and isolation of little or no 7*H*-benzocycloheptene 10 would be convincing evidence for direct formation of 14 (and thus cyclopropene trapping) in the cycloheptatrienylidene reaction with tetracyclone.

Toward this end, the product ratios via the two routes were checked under as nearly identical conditions of solvent and temperature as possible. Tropone tosylhydrazone salt was pyrolyzed in the presence of tetracyclone in a sealed tube with benzene as solvent at 100±5° (boiling water bath); diazo-2,3,4,5-tetraphenylcyclopentadiene in benzene (sealed tube) was photolyzed (550W, "Hanovia high pressure Hg vapor lamp," Pyrex filter) at 100±5° (boiling water bath) for an identical period of time. Products were quantitatively determined by gas chromatography (5% SE-30, 10'x1/8", 235°C), authentic samples of 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) for comparison being supplied by Mitsuhashi.[16] A mixture of the authentic materials was subjected to the thermolysis and photolysis reaction conditions and the stability of these products to reaction conditions demonstrated. Thus assurance

was obtained that the analysis procedure was truly indicative of the ratio of products formed.

Contrary to expectations identical ratios of 9:10 (1:4 molar ratio) resulted from the two reactions. Therefore a rapid cycloheptatriene--norcaradiene-bisnorcaradiene equilibrium results, and no clue as to the point of entry into the equilibrating system can be obtained from structures of final products.

Although a proof of cyclopropene trapping is obviated, these reactions offer entry into a series of very interesting intermediates and products. Tetraphenylcyclopentadienylidene addition to benzene gives as the major product 1,2,3,4,5-pentaphenylcyclopentadiene (16) along with the two 7*H*-benzocycloheptenes 9 and 10 (ratio of 16:9:10; 47:10:43). This confirms the proposal that an initially formed spiro-compound gives 16 thermally[18,21] and the benzocycloheptenes (11⇌12⇌13) photolytically.[17,18] High temperature photolysis at low photo-efficiency (i.e., higher concentration of diazotetra-



16 11

phenylcyclopentadiene and longer light path length of the irradiating light) offers a synthetically useful method for preparation of pentaphenylcyclopentadiene 16. Photolysis of the diazo starting material (0.50 g) in 40 ml benzene (sealed

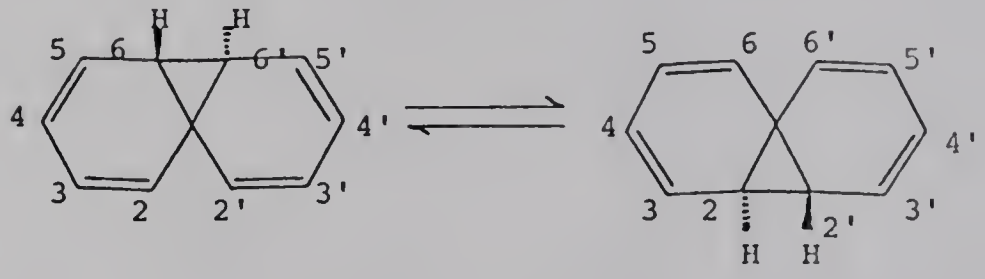
tube, twice the diameter of that employed previously) for 6 hours gave after recrystallization (ethanol) 0.39 g (68% yield) of the cyclopentadiene 16 (m.p. 248-252°, lit.[22,17] 244-246°, 247°, 254°) with spectral properties as reported.[22b]

The equilibrium constants for equilibration of the intermediates 11⇌12⇌13 are expected to be influenced by both substituents and temperature. Photolysis of the diazo starting material in benzene at 30° gives the 7*H*-benzocycloheptenes 9 and 10 in a ratio of 1:1 with no formation of pentaphenylcyclopentadiene 16. Thus temperature variation permits remarkable control of the products formed in the photochemical reaction.

The primary utility of these reactions is the access they provide to the unique norcaradiene-bisnorcaradiene intermediate 12. Although there are at least two other possible mechanisms that might be envisioned for interconversion of the 1*aH*-benzocycloheptenes 11 and 13 which by-pass 12, neither would be expected to be competitive with either [1.5]-hydrogen migration[20] or the cycloheptatriene--norcaradiene rearrangement which is known to be particularly facile[19] (E_{Act} <10 Kcal/mole). Thus, a concerted thermal [1.11]-sigmatropic rearrangement is forbidden (rearrangement must be thermal even if it can also be photochemical since the 11⇋12⇋13 equilibration occurs in the absence of light when entered via the cycloheptatrienylidene-tetracyclone reaction). Also, reversible ring opening to the severly crowded all *cis*-cycloundecahexaene (either by a concerted or a diradical

mechanism but occurring with or without photolysis) that could re-close to the rearranged product would hardly be expected to occur at temperatures as low as room temperature.

The norcaradiene-bisnorcaradiene 12 is a particularly intriguing molecule since it is not only capable of norcaradiene--cycloheptatriene isomerization but possibly of an unprecedented degenerate (without phenyl substituents) rearrangement as well. This rearrangement involves an orbital symmetry allowed antara-antara [5.5]-sigmatropic rearrangement with cleavage of C-6,6' and formation of a new sigma bond between carbons 2 and 2'. The molecular geometry of 12 is particularly well suited for this isomerization to



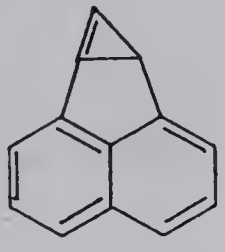
occur as a concerted rearrangement, particularly in light of destabilization predicted for the [5.5]-spirarene formed by homolytic cleavage of C-6,6'.[23] Unfortunately, the particular substitution pattern of 12 does not allow detection of this isomerization if it occurs. However, a number of substitution patterns that would permit detection can be devised.

CHAPTER II

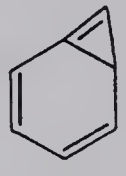
Destabilization of the Cyclopropene Intermediate: Carbene-Carbene Rearrangements in the Acenaphthylcarbene-Phenalenylidene System

A carbene specifically designed with structural features that destabilized a cyclopropene intermediate 5 should behave differently than a carbene with structural features that stabilize this intermediate. In particular, the former should be less prone to rearrangement if the cyclopropene 5 is truly an intermediate in these reorganizations. Were the cyclopropene 5 sufficiently destabilized, the mechanism of the rearrangement might be altered to avoid its intermediacy.

One means of destabilizing this intermediate would be to incorporate it into an abnormally small bicyclic system. A bicyclo[3.1.0]hex-5-ene (for example, 5d) should be substantially more strained than the more usual bicyclo[4.1.0]-hept-6-ene (for example, 5a, 5b, or 5c).[1] Therefore, 1-ace-



5d



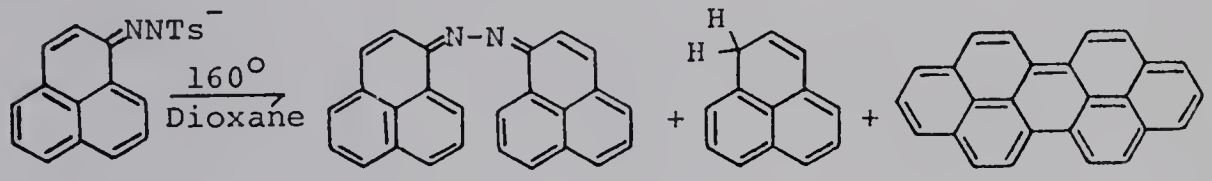
5a

naphthylcarbene (17) and 1-phenalenylidene (18) were chosen for a study of the effect of straining the cyclopropene intermediate, and how such destabilization influences the isomerization of these carbenes. Initially the experimental results left much to be desired due to the abnormal properties of phenalenylidene (18) and the small yield of carbene products detected. However, a recent report[24] has detailed the properties of carbene 18 and is compatible with these results.

Phenalen-1-one tosylhydrazone (19) was prepared from commercial phenalen-1-one (Aldrich) by the standard method[1] and had properties identical to those reported previously.[24,25] Acenaphthylene-1-carboxaldehyde (20) was synthesized from acenaphthylene by the Vilsmeir-Hack reaction.[26] This aldehyde was obtained in 24% yield as a solid (m.p. 55.5-57°, contrary to the report[26] that it is a liquid) which formed a semicarbazone with m.p. 241-243° (lit.,[26] 240°) and was oxidized to 1,8-naphthalic anhydride in the reported manner.[26] Acenaphthylene-1-carboxaldehyde tosylhydrazone (21) was obtained in the standard way.[1] Tosylhydrazones 19 and 21 were converted to sodium salts 19' and 21' with sodium hydride employing a method similar to that described previously.[1]

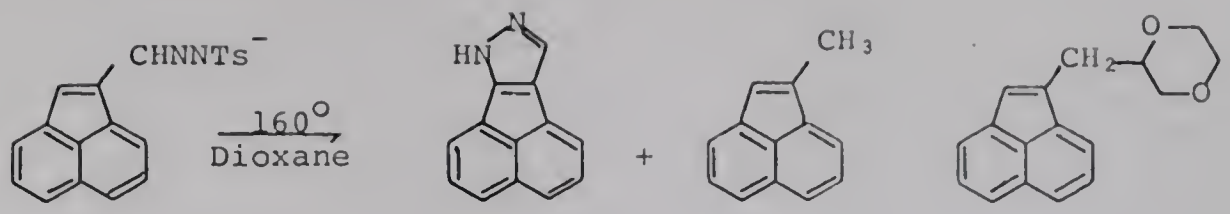
Thermolysis of phenalen-1-one tosylhydrazone sodium salt (19') in dioxane (sealed tube) at 160° produced phenalen-1-one azine (22) (ir, uv,[25] tlc identical to authentic material) as reported by others.[24] However, 22 was not completely stable to these reaction conditions and

its yield was irreproducible. Phenalene[24] (23) (6.9%; uv, nmr,[27] gc, tlc identical to authentic material[28]) was also isolated along with a small quantity of previously undetected peropyrene (Dibenzo[*cd*,*lm*]perylene, 24) (0.7%; uv-vis[29], gc, tlc identical with authentic material[30]). Due to the carcinogenic nature[31] of peropyrene (24), this compound was not isolated as the pure solid. Properties of dilute solutions left little doubt as to the identity of 24. Yields were determined by uv-vis spectrophotometry in benzene.[29]



19' 22 23 24

Thermolysis of acenaphthylene-1-carboxaldehyde tosylhydrazone sodium salt (21') under conditions similar to those employed for generation of phenalenylidene (18) gave about 50% nitrogen evolution and 7*H*-acenaphtho[1,2-*c*]pyrazole (25) (m.p. 238-241°, lit.,[32] 239°) as the major product. 1-Methylacenaphthylene (26) (7%, identical with authentic material[33] by uv and mass spectrometry) and a compound tentatively identified (nmr) as the dioxane insertion product of acenaphthylcarbene (27) (~3%) were also isolated. No trace of any common product could be detected by gas chromatography of the two reaction mixtures.

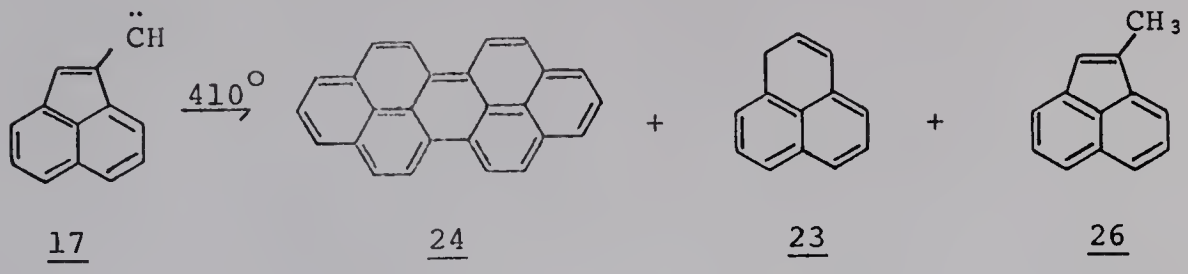


21' 25 26 27

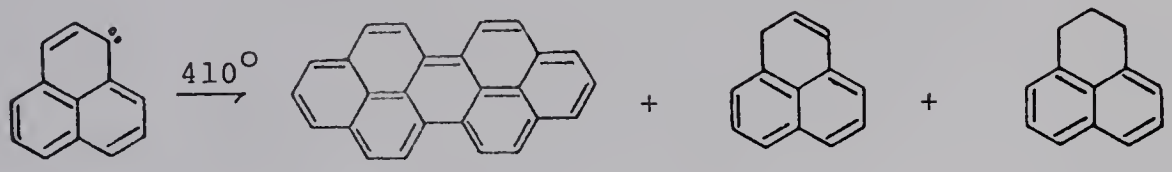
Hot tube pyrolysis under the conditions employed for isomerization of phenylcarbene (1) to cycloheptatrienylidene[1] (2) successfully effected rearrangement of the arylcarbene 17 to phenalenylidene (18) as evidenced by detection of peropyrene (24) and phenalene (23) in product mixtures. In fact, 23 and 24 were the major volatile products from hot tube pyrolysis of acenaphthylene-1-carboxaldehyde tosylhydrazone sodium salt (21') at 410° (5.3% 24, 3.2% 23, 1.8% 26 detected).

No acenaphthylcarbene products such as 26 were obtained from hot tube pyrolysis of phenalenylidene (18) (limit of detection 0.01% by gc). Unfortunately, reported yields from hot tube pyrolysis experiments may not be particularly informative since the low volatility of 24 may have resulted in some condensation prior to the trap. To avoid contact with 24,[31] this possibility was not experimentally tested. Hot tube thermolysis of phenalen-1-one tosylhydrazone sodium salt (19') at 410° gave peropyrene 24 and phenalene 23 as major volatile products along with a trace of 2,3-dihydrophenalene 28, identified by preparative gas chromatography followed by uv[28] and mass spectrometry (3.8% 24, 0.5% 23, 0.05% 28 detected). Isolation of 2,3-dihydrophenalene (28)

indicates a strongly reductive environment in the pyrolysis



17 24 23 26

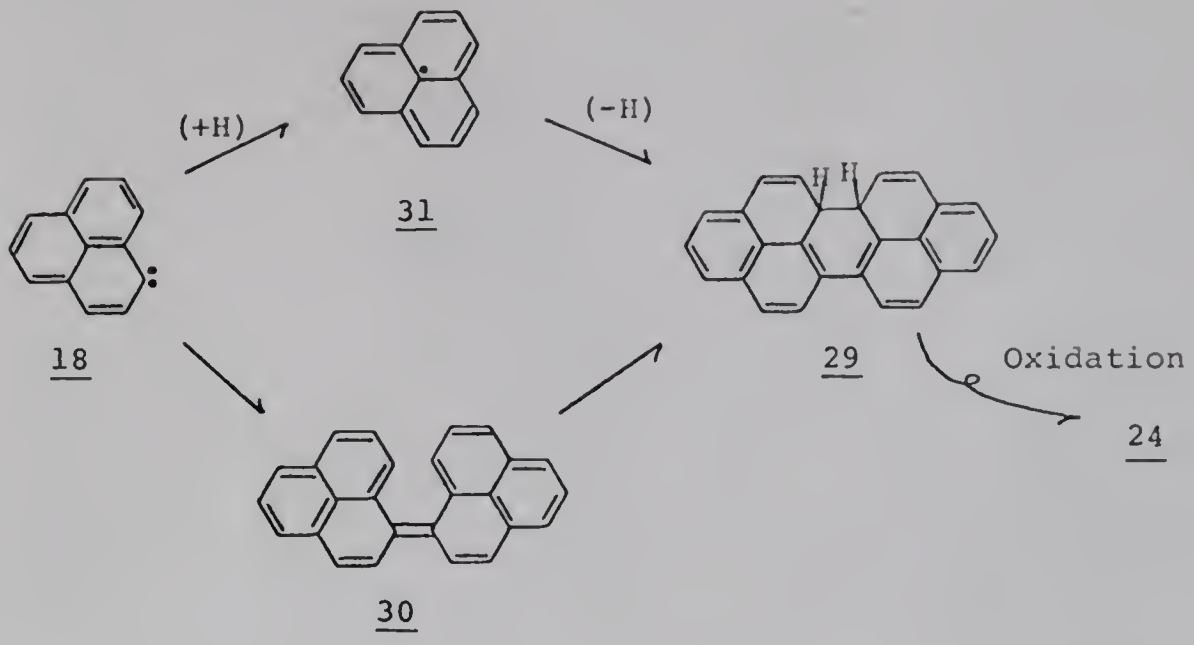


18 24 23 28

tube which may possibly be due to the transient presence of dihydroperopyrene (29) (a logical precursor of peropyrene). In addition, gas chromatography of both pyrolysis product mixtures shows products from sodium *p*-toluenesulfinate at various stages of reduction (thiocresol and tolyl disulfide detected by coinjection and minor components noted from the change in the chromatogram when the benzenesulfonylhydrazone salt of phenalen-1-one was pyrolyzed in place of 19').

The origin of peropyrene (24) (or its precursor 29) is not clear at this time. It could reasonably originate from either the carbene dimer 30 or the known[34] disproportionation of the phenalenyl radical 31 (a logical precursor of phenalene 23). In either event, it is apparent that acenaphthylcarbene (17) undergoes carbene-carbene rearrange-

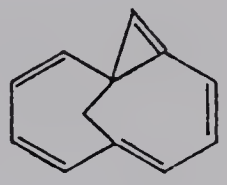
ment to phenalenylidene (18). In spite of the additional



strain on the cyclopropene intermediate 5d the rearrangement still occurs--this rearrangement being unique in that it is the first example of such an isomerization requiring expansion of a five-member ring. This result reinforces the previous indirect evidence implicating a cyclopropene intermediate since migration of only C-2 occurs (i.e., insertion is into the bond of higher π-bond order, or a preferable statement might be that the products result only from the more stable of the two possible cyclopropene intermediates or transition states). There is clearly no evidence for an obvious variation in the mechanism of rearrangement.

The comparable conditions for the rearrangement of acenaphthylcarbene (17) to phenalenylidene (18) and of phenylcarbene (1) to cycloheptatrienylidene (2) suggests that the lesser loss in resonance energy accompanying forma-

tion of the cyclopropene 5d (compared with formation of 5a) partially offsets the additional strain. However, the strain in 5d is apparently sufficient to prevent rearrangement in solution from being competitive with intermolecular processes. This is particularly pertinent since methano-10π-annulenylcarbene in which the cyclopropene intermediate 5e is incorporated into a much larger fused ring system undergoes



5e

rearrangement readily in solution.[5] Thus these results are completely consistent with rearrangement via a cyclopropene intermediate or transition state.

CHAPTER III

The Precursor to a Stabilized Cyclopropene Intermediate: Dibenzo[*a*,*c*]cycloheptatrienylidene; A Comparison of Its Properties with Those of Less Stabilized Intermediates

The most acceptable evidence for a cyclopropene intermediate 5 in a carbene-carbene rearrangement would be direct observation of this intermediate, or lacking that, trapping of the short lived species. With the observation of high yield rearrangements that occur in solution,[1,2,5] experiments with this aim were indicated. The cyclopropene, 5a, and the two carbenes, 1 and 2, have been estimated to be of similar energy.[9] However, it seems advantageous to choose carbenes interconvertible via an intermediate having the maximum energetic advantage (or, minimum energetic disadvantage) possible. The dibenzo[*a*,*c*]cycloheptatrienylidene-phenanthrylcarbene system was chosen since the intermediate, 5c, was expected to form with the least loss in resonance energy. Figure 4 gives an indication of the loss in resonance energy as the cyclopropene intermediate is formed from the arylcarbene or from the aromatic carbene. The resonance energy of the carbenes is taken to be equal to that of the respective cations, and the resonance energy of the intermediate is taken to be equal to that of the linear polyene with appropriate annelation. Delocalization energies are simple

Delocalization Energies

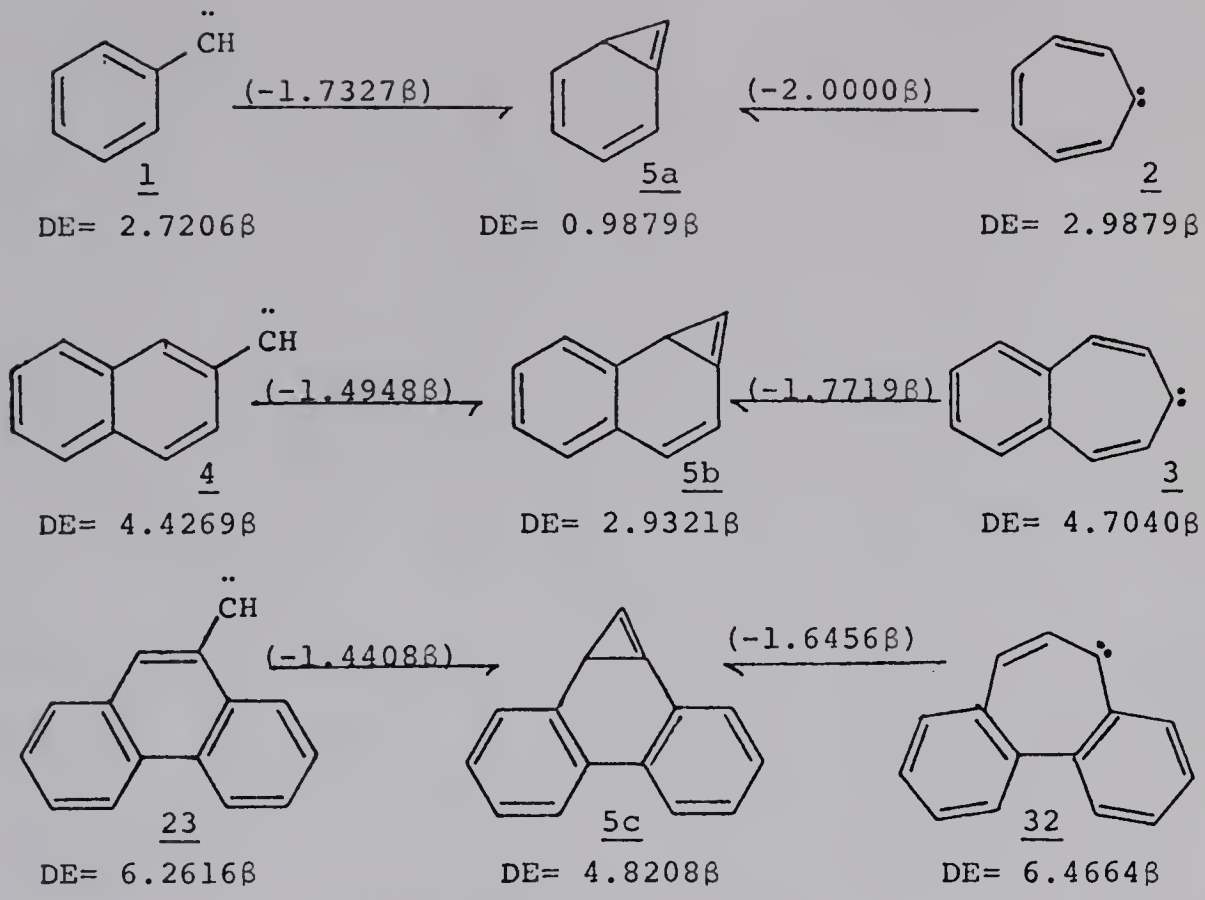


Figure 4

HMO values taken from Streitwieser's compilations.[35] Only differences between the three series are of significance. The advantage of choosing dibenzo[*a*,*c*]cycloheptatrienylidene (32) is obvious. Reactive dienes are expected to be appropriate trapping reagents for the strained cyclopropene 5c.[15]

Although dibenzo[*a*,*d*]cycloheptatrienylidene has been previously studied and found to behave as a diarylcarbene with no tendency to rearrange in solution,[36] dibenzo[*a*,*c*]-cycloheptatrienylidene 32 has not previously been reported. The preparation of this carbene and some of its reactions with particular attention to the similarities and differences

between carbene 32 and cycloheptatrienylidene 2 and 4,5-benzocycloheptatrienylidene 3, and the behavior of these carbenes in the presence of dienes were examined for the implication of a cyclopropene intermediate.

5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one (38) was required for the preparation of the carbene 32. Prior methods of synthesis[37,38] appeared too troublesome or expensive. Therefore, a synthetic sequence (Figure 5) based on a method for preparation of 6-chloro-5*H*-dibenzo[*a*,*c*]cycloheptene previously developed by Waali and Jones[39] was employed. A procedure similar to that reported by Joshi, Singh, and Pande[40] allowed the accumulation of a large quantity of 7,7-dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (34). The alcohol 35 was obtained in quantitative yield by heating a melt at 170° for 30 minutes, and then cooling and hydrolyzing the resultant oil with aqueous acetonitrile containing sodium bicarbonate. Isomerization of the alcohol 35 to the chloroketone 37 was most conveniently accomplished by oxidation with activated manganese dioxide to the unsaturated chloroketone 36[41,42] (90% yield) followed by catalytic reduction (78% yield).

Hydrogenolysis accompanies hydrogenation and occurs especially rapidly in ethanol. In fact, catalytic reduction of the unsaturated chloroketone 36 with two equivalents of hydrogen in ethanol appears to be the method of choice for synthesis of 6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (39).[37,43,44] Ketone 39 was obtained in 82% yield from a small scale initial reaction with no effort to maximize the

Synthetic Scheme

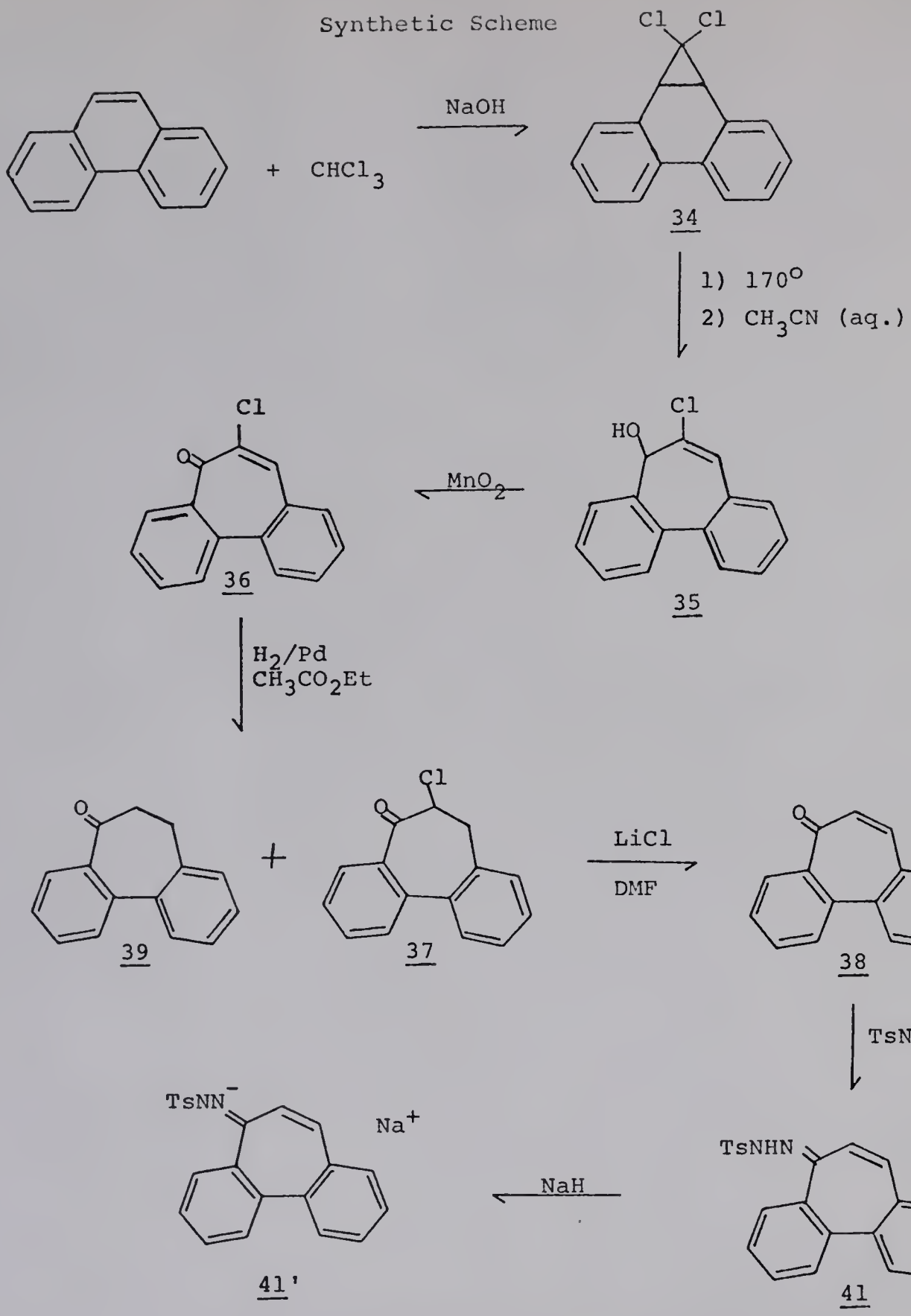


Figure 5

yield. The ratio of 37 to 39 depends on the extent of reduction, the nature of the solvent, and the acidity of the solvent. Factors which were not evaluated may also play a role. Table 1 shows the ratio of 37 to 39 when 1.1 equivalents of hydrogen were introduced and the reduction was carried out in a number of different solvents. Fortunately, when ketone 39 is formed as an undesirable side product, it can be brominated[44] and the bromoketone 40 used in place of chloroketone 37 in the subsequent step.

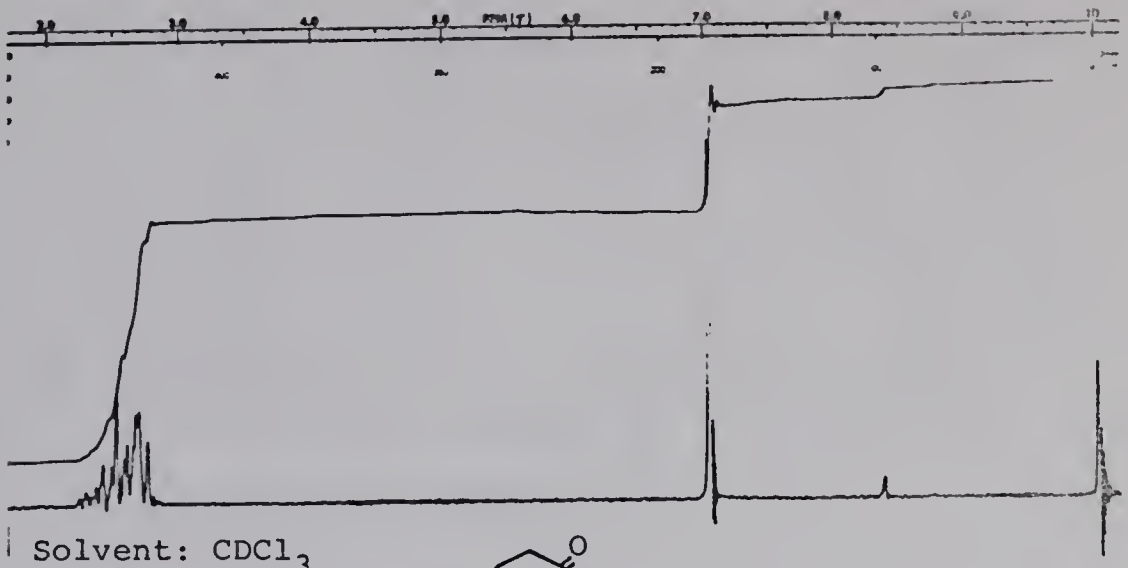
Table 1

Solvent Effect on the Reduction of 6-Chloro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (36)

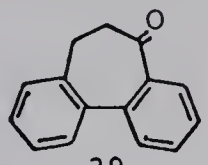
Solvent	37/39
Ethylacetate (1% HOAc)	5.2
Glacial Acetic Acid	3.0
Benzene/50% Cyclohexane	0.9
Ethanol	0.3

Both ketone 39 and chloroketone 37 have unusual nmr spectra which exhibit remarkable variation with solvent. In $CDCl_3$ the spectrum of 39 shows only aromatic protons and a sharp singlet at τ 7.00; in benzene-d_6, the upfield singlet becomes the expected AA'BB' multiplet. In benzene-d_6 the 60 MHz nmr spectrum of chloroketone 37 shows aromatic protons, a sharp triplet at τ 4.62, and a sharp doublet at τ 7.05 (J=7.5 Hz); in acetone-d_6, the spectrum is the textbook ABX pattern (ν_A= τ 6.81, ν_B= τ 6.48, ν_X= τ 4.11, J_{AB}=13.5 Hz, J_{AX}=9.0 Hz, J_{BX}=4.5 Hz); the 60 MHz spectrum in CCl_4 has accidental coincidences that make the ABX pattern somewhat less obvious (ν_A= τ 6.84, ν_B= τ 6.61, ν_X= τ 4.52, J_{AB}=13.5 Hz,

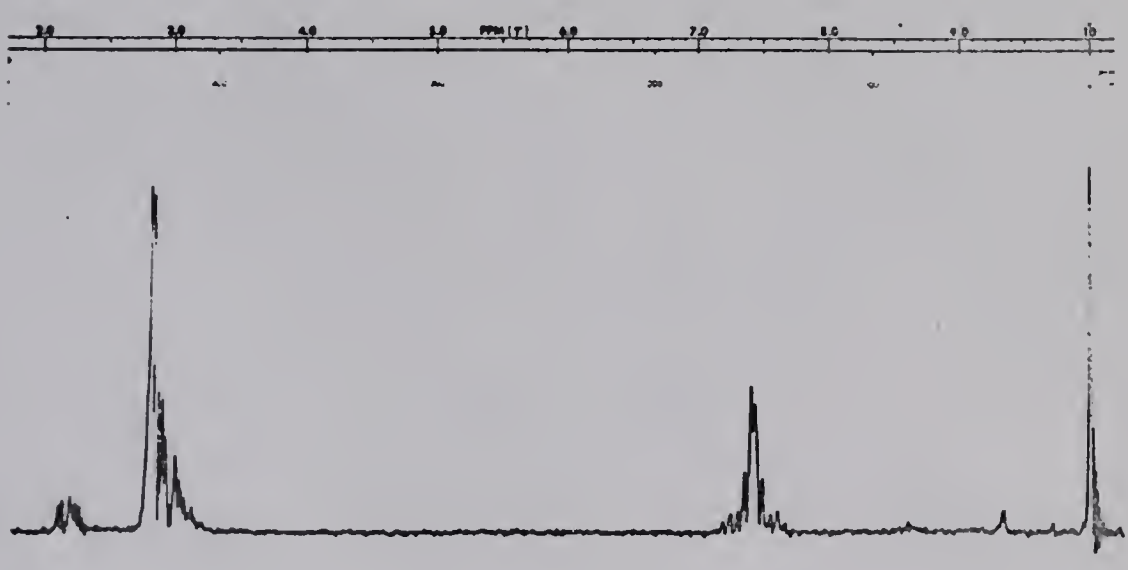
Nmr Spectra of 39



Solvent: $CDCl_3$



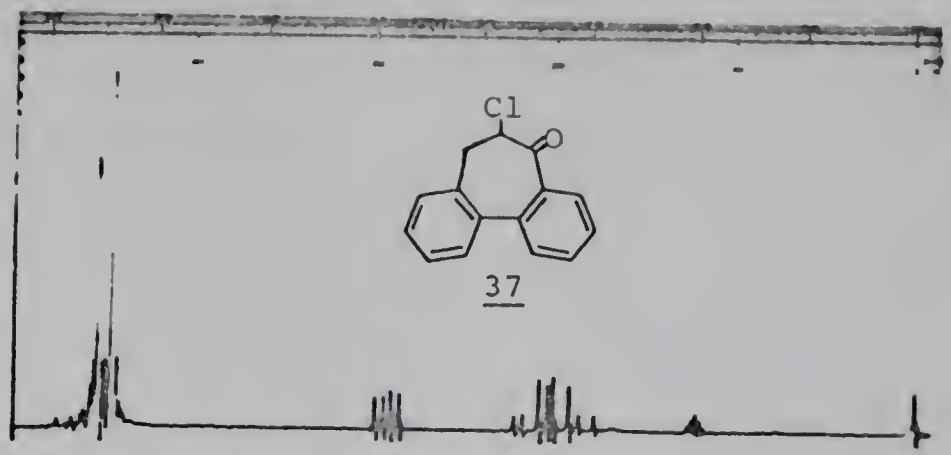
39



Solvent: C_6D_6

Figure 6a

Nmr Spectra of 37



37

Solvent: Acetone-d_6

Solvent: CCl_4

Solvent: C_6D_6

Figure 6b

J_{AX}=12. Hz, J_{BX}=3. Hz). Spectra in various solvents are shown in Figure 6a (6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (39)) and Figure 6b (6-chloro-6,7-dihydro-5*H*-dibenzo-[*a*,*c*]cyclohepten-5-one (37)). These two products of the same reaction offer an amusing nmr study. It is particularly notable that in spectra of the chloroketone 37 coupling constants as well as chemical shifts vary with solvent, presumably due to a different average molecular conformation in each solvent. Since $J_{AX}=J_{BX}$ in benzene-d_6, chloroketone 37 apparently assumes an average conformation in which the H_a-H_x dihedral angle is identical to the H_b-H_x dihedral angle (i.e., H6 is, on the average, perfectly staggered between the two H7 protons) in this solvent.

Dehydrohalogenation to the desired ketone 38 is readily accomplished under conditions similar to those employed by Collington and Jones[45] for the preparation of other tropones. Spectral and physical properties of the final product (38) are identical in all respects to the ketone 38* prepared in a standard way.[37] Conversion to the tosylhydrazone (41) and formation of the tosylhydrazone sodium salt (41') were carried out under conditions similar to those reported.[1] The carbene 32 was generated from the salt by pyrolysis or by Pyrex filtered photolysis.

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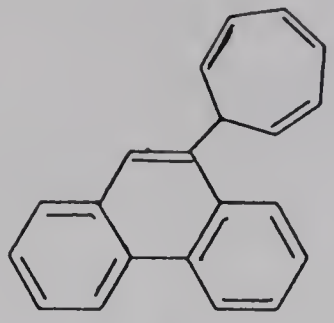
* Authentic 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (38) was prepared by Dr. P. Mullen.

Dibenzo[*a*,*c*]cycloheptatrienylidene 32 mimics the monoannelated cycloheptatrienylidene 3 in its facile rearrangement when thermally generated in solution.[1,2] In benzene at 125° it rearranges cleanly and forms 9-(2,4,6-cycloheptatrien-1-yl)-phenanthrene (42) quantitatively. Photolytic

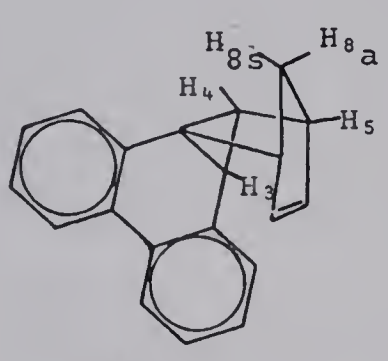


42

generation at room temperature in benzene also produces the phenanthrylcarbene addition product 42 as the major product, although the yield is less than quantitative. The rearrangement seems to be rather sluggish when the aromatic carbene 32 is formed photolytically at -60° in 1:2 benzene-tetrahydrofuran. Less than 0.2% yield of the phenanthrylcarbene addition product to benzene 42 is isolated. Other work with phenanthrylcarbene 33 under these conditions indicates a similar amount of tetrahydrofuran insertion products also form.[46] The nmr spectrum of the product mixture obtained when dibenzo[*a*,*c*]cycloheptatrienylidene 32 is photolytically generated at -60° in tetrahydrofuran in the absence of any other reactant indicates largely aromatic material with less than 10% yield of compounds containing the phenanthrene moiety. Yet, rearrangement is certainly occurring to a small but significant degree (0.05 to 10%) even at these low temperatures.

The aromatic carbene 32 does not, however, react with olefins prior to rearrangement as do other aromatic carbenes such as 4,5-benzocycloheptatrienylidene[1,2] 3 and cycloheptatrienylidene 2.[47,48] Even at temperatures so low that products from the rearranged carbene 33 were isolated in only very low yield, no evidence for the spiro-adducts to styrene or dimethyl fumarate could be obtained. The products observed from photolysis of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt 41' in tetrahydrofuran at -60° with an olefinic trap present were similar to those obtained in the absence of a trap. This is unexpected since carbenes 2 and 3 give spiro-adducts with dimethyl fumarate and styrene under these conditions.[47-49]

However, a reactive species can be trapped with dienes. Photolysis of the sodium salt of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone 41' at -60° in the presence of cyclopentadiene or furan with dry tetrahydrofuran as co-solvent gives the Diels-Alder adduct of the cyclopropene intermediate 5c with the diene, *endo*-2,3-(*o*-biphenylenyl)-tricyclo-[3.2.1.$0^{2,4}$]oct-6-ene (43) or 1,7-(*o*-biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (44), respectively (73% and 47% yields).



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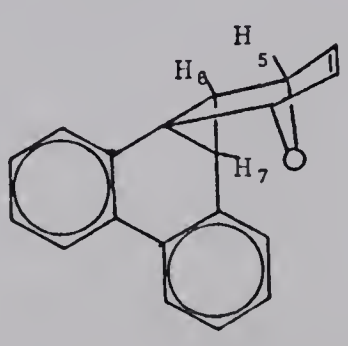

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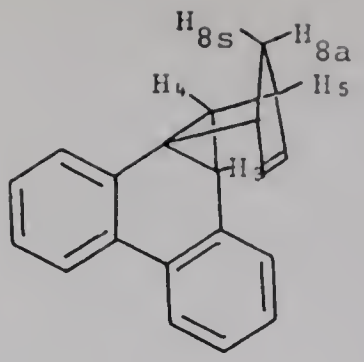

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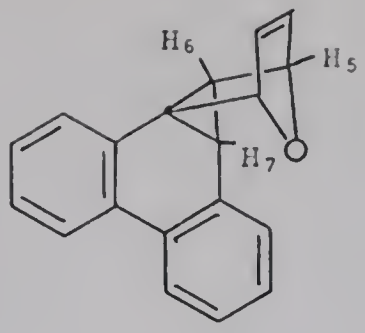
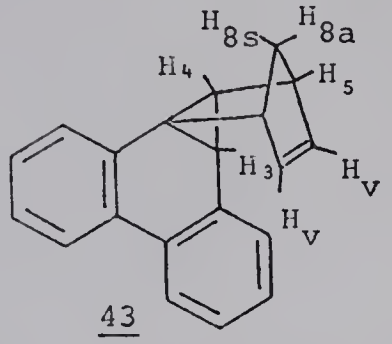


44

As long as the photolysis is stopped shortly after all the tosylhydrazone salt 41' has decomposed, adduct 43 is the only isomer found to a limit of detection of about 1%. The spectral properties leave little doubt that it is the *endo* isomer. An ir band at 1045 cm^{-1} indicative of a cyclopropane ring is observed.[50] The magnitude of the coupling constant for the vicinal cyclopropane hydrogens, $J_{3,4}$=2.8 Hz, requires they be positioned *trans* on a tricyclo[3.2.1.$0^{2,4}$]-octane structure,[50-52] and the H4 chemical shift (τ 9.39) demands that this proton (H4) lie on the same side of the cyclopropane ring as the aromatic substituent[53]--this being, of course, the only rational geometry (these features are also apparent in the spectrum of the furan adduct 44). The *endo* structure for 43 is also suggested by the magnitude of the H4 cyclopropane hydrogen coupling to the adjacent bridgehead proton, $J_{4,5}$=2.6 Hz, which is of the appropriate magnitude only if the H4 proton is *exo*. Consistent with a *trans* orientation of H3-H4, H3 must be *syn*. This is certainly the case since were H3 *anti*, long range coupling to $H8_{anti}$ would be expected.[50,54] The very sharp doublet

observed for H3 ($J_{3,4}$=2.8 Hz, only) even in an expanded 100.1 MHz spectrum and the lack of any sharpening of this signal when either methylene bridge proton is irradiated belies the possibility that H3 is *anti*. The vinyl protons appear as a narrow multiplet approximating a triplet (60 MHz) in adduct 43, at τ 3.95, significantly upfield from vinyl protons observed in spectra of known tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene compounds with the cyclopropane ring *exo*, but



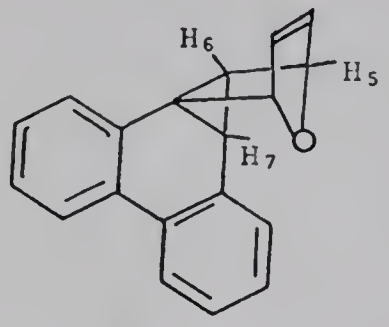
43

consistent with an *endo* structure.[50] The high field position of the cyclopropyl hydrogen H3 at τ 7.49 requires that it be *syn* on an *endo* ring.[55] The best model for this compound is *endo*-2,3,4-triphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene with the 3-phenyl *anti*.[55] In its nmr spectrum the vinyl protons appear at τ 3.77 and the *syn* cyclopropane hydrogen at τ 7.53, in line with spectrum of adduct 43. Finally, the similar chemical shifts of the methylene bridge protons, $H8_{syn}$ and $H8_{anti}$, suggest that the cyclopropane ring is not in near proximity to these protons.

Unassailable proof that the isomer formed (43) has the *endo-anti* configuration is essential to the contention that this compound results from a Diels-Alder reaction of the

cyclopropene intermediate 5c with cyclopentadiene. There is no example of the formation of any stereoisomer other than the *endo-anti* isomer in cycloaddition reactions of 3-monosubstituted cyclopropenes with cyclopentadiene.[15,50,55,56]

Spectral evidence is equally convincing in support of an *endo*-epoxy structure for 44, the major product formed on reaction with furan. However, this reaction is not as clean as that with cyclopentadiene. A number of unidentified minor products (including at least three products from subsequent photolysis of 44) are always obtained along with 44. A small



44

amount of the *exo*-epoxy isomer, which would presumably be the less stable isomer,[57] may have escaped detection, although currently there is no evidence for its formation. There are a number of previous reports of cyclopropenes reacting with furans to yield only the *exo* adduct.[58-60] The structure assignment rests on the absence of coupling of the cyclopropyl proton H6 with the adjacent bridgehead proton, H5, as expected if H6 is *endo* on the oxy-norbornene portion of the molecule,[57,58] and on the abnormally low field position (τ 6.39) of the cyclopropyl proton H7 which suggests its proximity to the bridging oxygen[59,60] (cf., the analogous

proton at τ 7.49 in 43). The molecule 44 is also particularly well suited for structure determination by an analysis of lanthanide-induced proton nmr shifts. The result of addition of a small amount of $Eu(fod)_3$ to an nmr solution containing adduct 44 is shown in Figure 7. A dramatic down field shift of the cyclopropyl hydrogen H7 of even greater magnitude than that experienced by the alkoxy protons at the bridgehead positions occurs. (All these protons are situated at a similar angle to the Eu-O contact line.) A rough calculation of the agreement factor[61] for the *exo*-epoxy isomer (R=0.36) and for the *endo*-epoxy isomer (R=0.05) provides convincing evidence that the molecular geometry is that claimed (the lanthanide atom was assumed to be directly above the oxygen in the plane bisecting the bridge at a distance of 3.Å; distances and angles were measured manually from a Dreiding Model. Only nonaromatic protons were used in the computation and only shift data from the spectrum at maximum mole ratio $Eu(fod)_3$:44).

Although good yields of adducts 43 and 44 are obtained at low temperatures, and volatile and reactive dienes are most conveniently employed below room temperature, the formation of these adducts is possible at any temperature at which the aromatic carbene 22 undergoes rearrangement. Photolysis of the tosylhydrazone salt 41' at room temperature in neat furan produces 43% yield of the adduct 44. Yields from the low temperature and the room temperature photolysis experiments are quite comparable considering the scale on which these reactions are run. Also, pyrolysis at

Nmr Spectra of 44 with Increasing Amounts of $Eu(fod)_3$ Present.

44

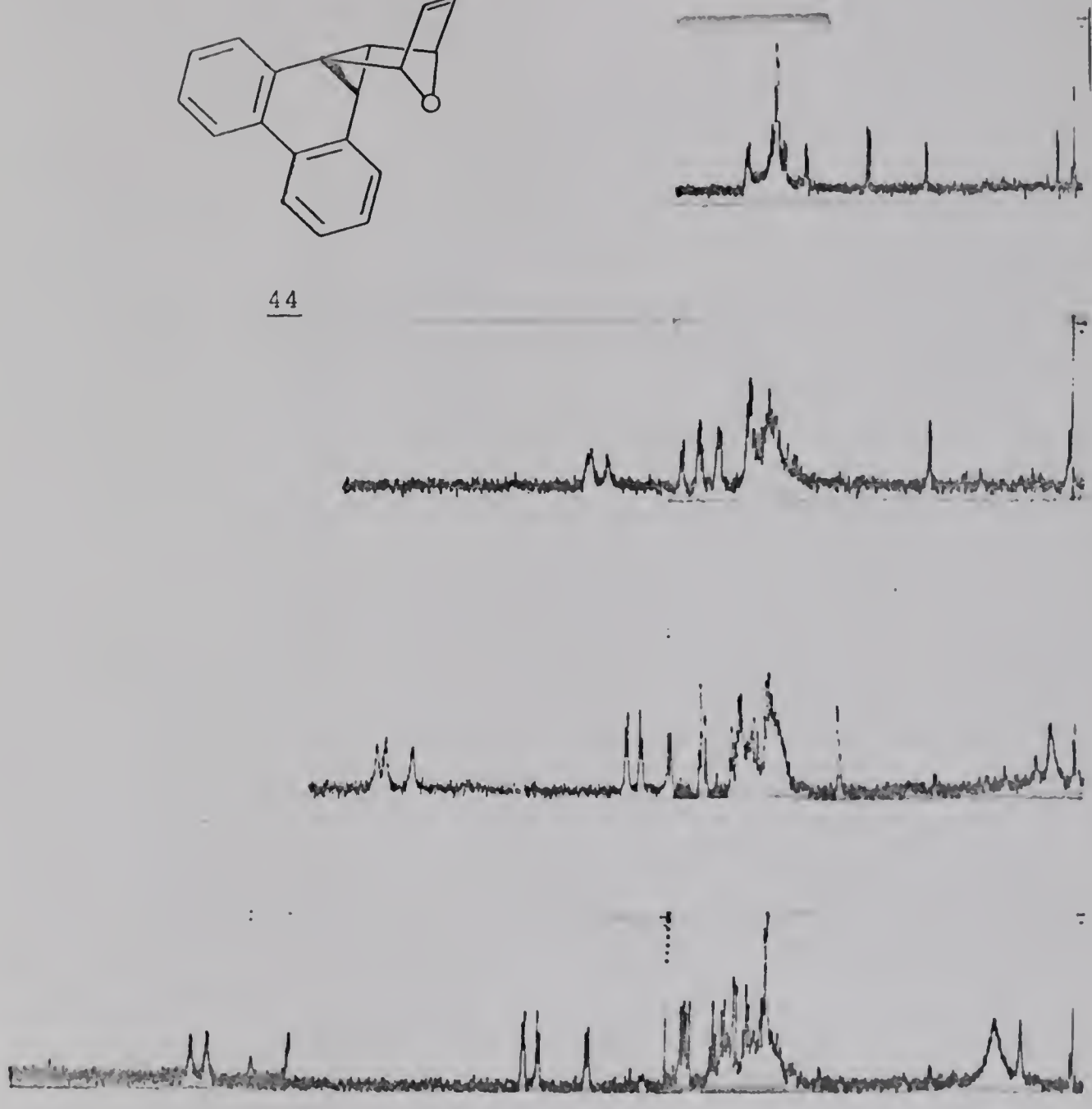
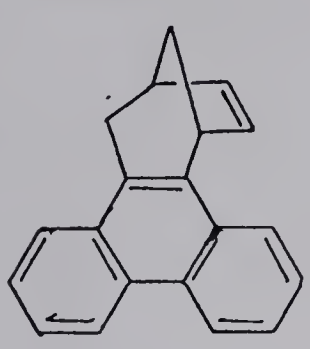
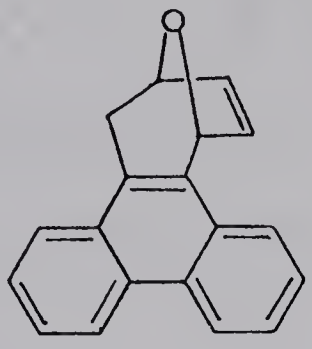
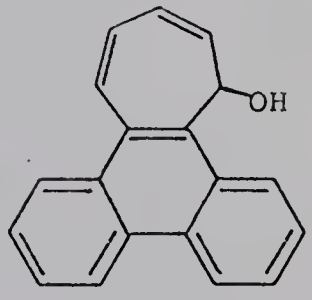


Figure 7

115° gives 11% of this furan adduct 44. In each case the *endo*-epoxy isomer of 44 is formed with no indication that any *exo*-epoxy isomer is generated. Unfortunately, adduct 44 is thermally unstable at the temperature necessary for thermal formation of carbene 32. 43 is also photolytically unstable. The primary result of thermolysis (and a minor product from photolysis) of adducts such as 43 and 44 appears to be structures formed by cleavage of the most strained cyclopropane ring bond (for example, 10,13-methano-9*H*-cyclohepta[*l*]phenanthrene and 10,13-epoxy-9*H*-cyclohepta-[*l*]phenanthrene). Excessive photolysis of 44 produces three







44'

products and an intractable residue. The major product seems to be a phenanthrene fused alcohol (possibly 44') in 40-60% yield along with two minor products (10-15% yield), one of which is similar to the major pyrolysis product. However, these are only tentative structure assignments based solely on nmr spectra. Such secondary thermal and photolytic products offer little relevant information pertaining to the question at hand. Though perhaps it should be mentioned that thermal generation of phenanthrylcarbene 33 from the aldehyde tosylhydrazone sodium salt 45' gives different major products. This suggests efficient trapping of the

cyclopropene 5c in high as well as low temperature rearrangements, but with extensive thermolysis of the initially formed adduct (presumably 44) at high temperatures. Since some of the adduct 44 can be isolated from thermal as well as photolytic generation of the carbene 32, this product clearly cannot be the result of a secondary photo process.

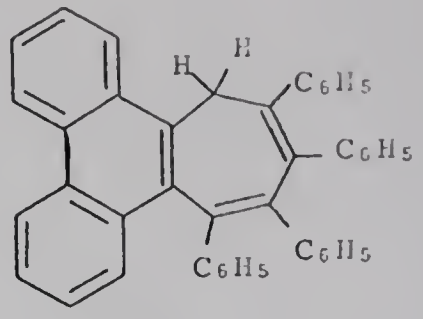
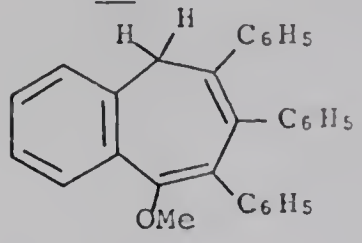
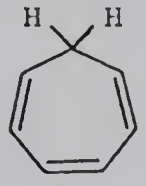
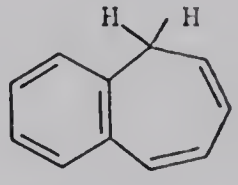
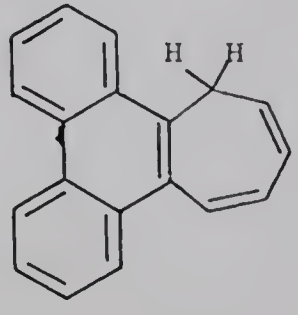
Trapping of the cyclopropene intermediate 5c under high temperature conditions is best accomplished employing 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) in a reaction modeled after that developed by Mitsuhashi in studies with cycloheptatrienylidene 2.[16] Excess tetracyclone must be destroyed by a cycloaddition with propiolic acid followed by removal of acidic components, since the products and tetracyclone cannot be separated directly by column chromatography or preparative layer chromatography. 10,11,12,13-Tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46) is the major product in about 50% yield contaminated with a trace of 9,10,11,12-tetraphenyl-11*H*-cyclohepta[*l*]phenanthrene (47) or possibly 9,10,11,12-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (47'). The proposed structure of the minor impurity is suggested by the nmr spectrum (τ 4.52 for the methine proton) which is as expected for a compound with a structure analogous to the major product 10 which forms on reaction of cycloheptatrienylidene 2 with tetracyclone (τ 4.63 for the methine proton[16]). A clear differentiation between the two possible isomers 47 and 47' is not possible, although additional work permitted an unambiguous assignment in the cycloheptatrienyli-

case. The principal product 10,11,12,13-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46) is apparently the most stable hydrogen shift isomer and is formed by acid catalyzed, base catalyzed or thermal isomerization of less stable isomers. The structure of this compound is clear from its spectral properties. The uv spectrum shows the very weak longest wavelength absorption so characteristic of phenanthrene at λ_{max} 357 nm with shorter wavelength bands obscured by the tail of a more intense absorption due to another chromophore in the molecule. The nmr spectrum shows the underside protons on phenanthrene at τ 1.25-1.6 (m, 2H) just as expected (phenanthrene itself also has these protons at τ 1.25-1.6 (m, 2H)[62]). The coupling constant J=12.5 Hz is consistent with that generally observed for geminal coupling in conformationally restricted cycloheptatrienes,[63] azepines, and diazepines.[64] It is inconsistent with $J_{1,7}$ which is generally 6.0-7.5 Hz and any long range coupling. Table 2 compares the H-nmr spectral properties of 10,11,12,13-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46) with appropriate model compounds.

9-Methoxy-6,7,8-triphenyl-5*H*-benzocycloheptene[63] is a particularly good model for the product obtained in this reaction. It, also, is apparently the most stable isomer and is prepared from 5-methoxy-6,7,8-triphenyl-5*H*-benzocycloheptene by thermal isomerization. Heating either isomer in refluxing xylene results in a mixture of the two isomers. Likewise, heating 10,11,12,13-tetraphenyl-9*H*-cyclohepta[*l*]-

Table 2

Nmr Spectral Properties of 46 and Similar Compounds

Compound	$H_{eq}(\tau)$	$H_{ax}(\tau)$	J_{gem}	T_c	Reference
 46	5.38	6.08	12.5 Hz	>150°	this work
	6.27	6.50	12 Hz	65°	63
	7.1	8.5	11 Hz	-143°	64 & 65
	7.10 (d, $J_{1,7}$= 7.0 Hz)				66
	6.24 (d, $J_{1,7}$= 6.2 Hz)				17

phenanthrene 46 in refluxing xylene produces some of the isomeric compound (47 or 47') with an nmr signal at τ 4.52 along with a good deal of material(s) with totally aromatic protons. Preparative layer chromatography or recrystallization (chloroform) fails to give a pure material.

Heating 10,11,12,13-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene 46 in an nmr spectrometer (tetrachloroethylene as solvent) results in a distinct loss in spectral resolution at about 150±10°. However, an average spectrum is never observed at higher temperatures. On cooling to room temperature, a mixture of compounds similar to those that result on refluxing in xylene is observed. The model compound 9-methoxy-6,7,8-triphenyl-5*H*-benzocycloheptene also has a high nmr coalescence temperature (65°) for the ring flipping process that averages the axial and equitorial proton signals. 9*H*-Cyclohepta[*l*]phenanthrene 46 would be expected to have a substantially higher nmr coalescence temperature, and it is not surprising that a temperature in excess of 150° is required. However, with 46 the nmr coalescence temperature is not necessarily due to conformational isomerization, but may rather be a result of rapid hydrogen shifts or some other process.

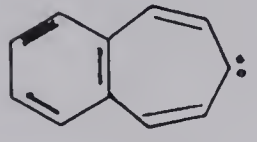
The intermediate (presumably the cyclopropene 5c) which reacts with dienes to produce these adducts has a sufficient lifetime to be detected even after photolysis, and hence generation of the initial intermediate 32 has ceased. The halflife of the reacting species 5c is of the order of a few minutes at -60° as determined by very crude late addition

experiments using cyclopentadiene. After photolyzing 41' seven minutes at -60°, the light was extinguished and cyclopentadiene (at -78°) was added immediately to give a 4.7% yield of adduct 43; a similar photolysis with addition of the diene two minutes after photolysis ceased gave a 3.6% yield of 43. It is unlikely that steady-state conditions were achieved or that temperature, light intensity, and other reaction variables were sufficiently similar to allow more than a rough estimate of the halflife (ca. 6 minutes if first order; ca. 7 minutes if second order). A rough minimum activation energy for formation of the arylcarbene 33 from cyclopropene 5c would therefore be at least 11 kcal/mole (an approximate frequency factor is taken from a similar cyclopropene fission[67]). The activation energy is probably somewhat greater since it is doubtful that 5c entirely decomposes via the arylcarbene 33.

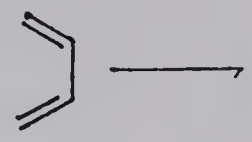
4,5-Benzocycloheptatrienylidene 3 is the premier example of an aromatic carbene that rearranges to an arylcarbene in solution and has been extensively studied.[1,2] At low temperatures in the presence of olefins spiro-compounds result from trapping of the aromatic carbene 3. Although the yield is poor, cyclohexene,[1,2] dimethyl fumarate, styrene, and substituted styrenes successfully react with this aromatic carbene.[49] As the temperature is raised, the yield of products resulting from the rearranged carbene, β-naphthylcarbene (4), improves.

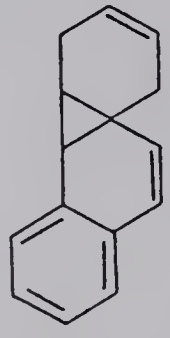
If a cyclopropene intermediate is required for rearrangement, it should also be possible to trap such an intermediate from this carbene (3). When 4,5-benzocycloheptatrienylidene (3) was formed in the presence of the diene, 1,3-cyclopentadiene, by low temperature photolysis, a small amount (16% yield) of *endo*-5,6-benzotetracyclo[7.2.1.$0^{2,7}$.$0^{2,8}$]dodeca-3,5,10-triene (48) resulted. This is just the product expected from reaction of the cyclopropene intermediate 5b with cyclopentadiene in a Diels-Alder reaction. The molecular geometry of this adduct follows from a comparison of its spectra with those of the adduct 43 obtained from dibenzo-[*a*,*c*]cycloheptatrienylidene (32) and cyclopentadiene. Table 3 (on the following page) compares nmr spectra of 43 and 48. A structure argument similar to that presented for adduct 43 based on nmr spectral data can also be developed for this adduct.

Reaction of 4,5-benzocycloheptatrienylidene (3) with 1,3-butadiene at low temperatures produces a number of isomeric hydrocarbons. The major product is 4,5-benzotricyclo[5.4.0.$0^{1,6}$]undeca-2,4,9-triene (49), and a minor

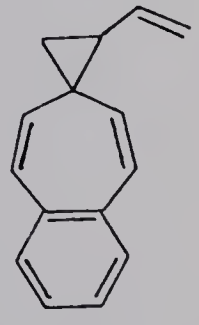


3





49



50

Table 3

Nmr Spectra (τ)

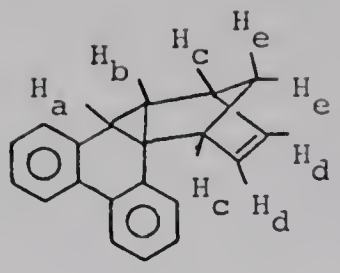
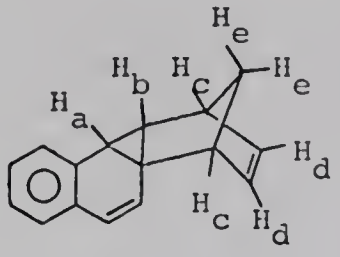
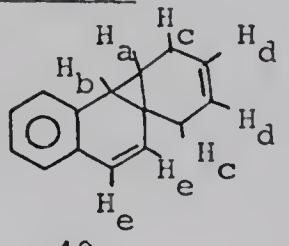
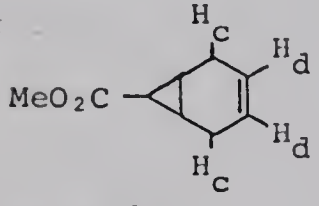
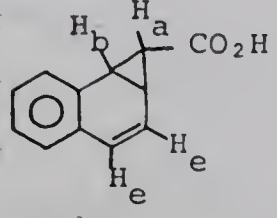
	H_a	H_b	H_c	H_d	H_e
 43	7.49	9.39	6.61 6.89	3.95	7.73 8.10
	J_{ab}=2.8 Hz, J_{bc}=2.6 Hz, $J_{ee'}$=6.8 Hz				
 48	7.52	9.65	6.93 7.05	4.1	7.9 8.18
	J_{ab}=2.8 Hz, J_{bc}=2.6 Hz, $J_{ee'}$= 6.8 Hz				

Table 4

^{1}H-nmr (τ)[68]

Compound	H_a	H_b	H_c	H_d	H_e
 49	9.45- 9.75(m)	7.64(d) J_{ab}=4.7 Hz	7.47	4.35- 4.55	3.84
			7.6	4.5	
	9.15	6.90			3.62
	$J_{a,b}$=4.1 Hz				$J_{e,e'}$=10.1 Hz

product is the spiro-compound expected from addition of the aromatic carbene to one double bond of the diene, 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (50). The spectral and physical properties of the adduct 49 are just as anticipated for a benzonorcaradiene incorporated into a 3-norcarene.[68] Table 4 (on the preceding page) lists the nmr spectral features. The nmr spectrum has cyclopropane protons with chemical shifts and coupling constants just as observed in the nmr spectra of other similar adducts (cf., spectra of 43, 44, 48, and 49 in Figure 8). Also, the spectral properties of the spiro-isomer 50 are consistent with those of other similar 6,7-benzospiro[2.6]nona-4,6,8-trienes.[1,2,49] In fact, there are amazing similarities between the ir spectrum of 50 and that of 1-phenyl-6,7-benzospiro[2.6]nona-4,6,8-triene[49] (as well as other analogous phenyl substituted compounds). Nmr spectra of spiro-products obtained on addition of cycloheptatrienylidene (2) to olefins[47,48] also agree well with the spectrum of 50. Pertinent nmr spectral features along with similar features in model compounds are collected in Table 5.

With 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (50) in hand, it is possible to offer evidence against one possible objection to a cyclopropene trapping mechanism for formation of the major isomer 49. Cycloheptatrienylidene (2) has been shown to react with the diene, *cis*-1,3-pentadiene, to yield 1-propenylspiro[2.6]nona-4,6,8-triene which rearranges

^{1}H-nmr Spectra of Adducts

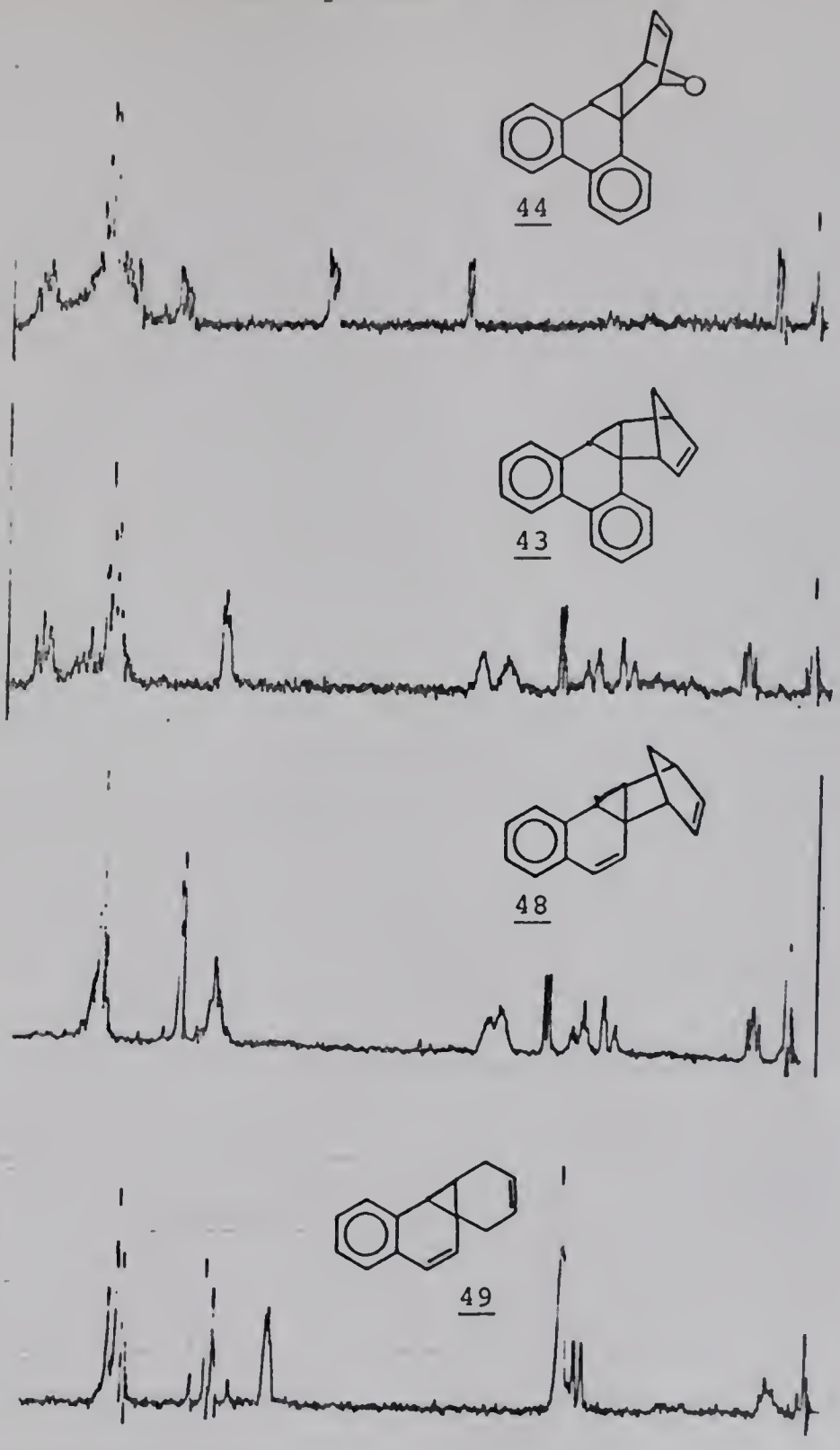
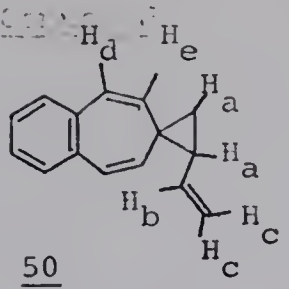
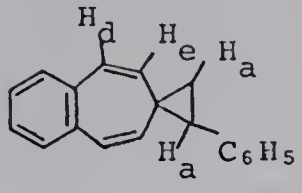
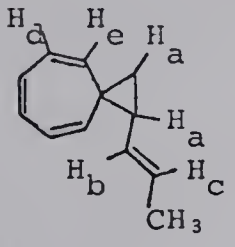


Figure 8

Table 5

Nmr Spectral Properties of 50 and Similar Compounds

Compound	$H_a(\tau)$	$H_b(\tau)$	$H_c(\tau)$	$H_d(\tau)$	$H_e(\tau)$
 50	8.25-9.2	4.2-4.8	4.75-5.2	3.72 3.84 J_{de}=11.5 Hz	4.75-5.2
	8.45-8.8			3.73 3.84 J_{de}=11.5 Hz	4.82 5.31
	8.55-9.05 and 9.40	4.5-5.3			3.5-4.2

thermally to 8-methylbicyclo[5.4.0]undeca-1,3,5,9-tetraene[48] (Figure 9a). A similar mechanism with cycloheptatriene to norcaradiene isomerization can be ruled out as a possible mode of formation of 49 since 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (50) is thermally stable to molecular distillation at 70°. It also fails to undergo conversion to 49 when subjected to the photolysis and workup conditions under which adduct 49 is obtained (to a limit of detection of better than 1%, ca. 75% of starting material being recovered). Thus the adduct 49 cannot be formed from 50 by a secondary reaction (Figure 9b) of either a thermal or photochemical nature.

A Two-Step Mechanism for Adduct Formation

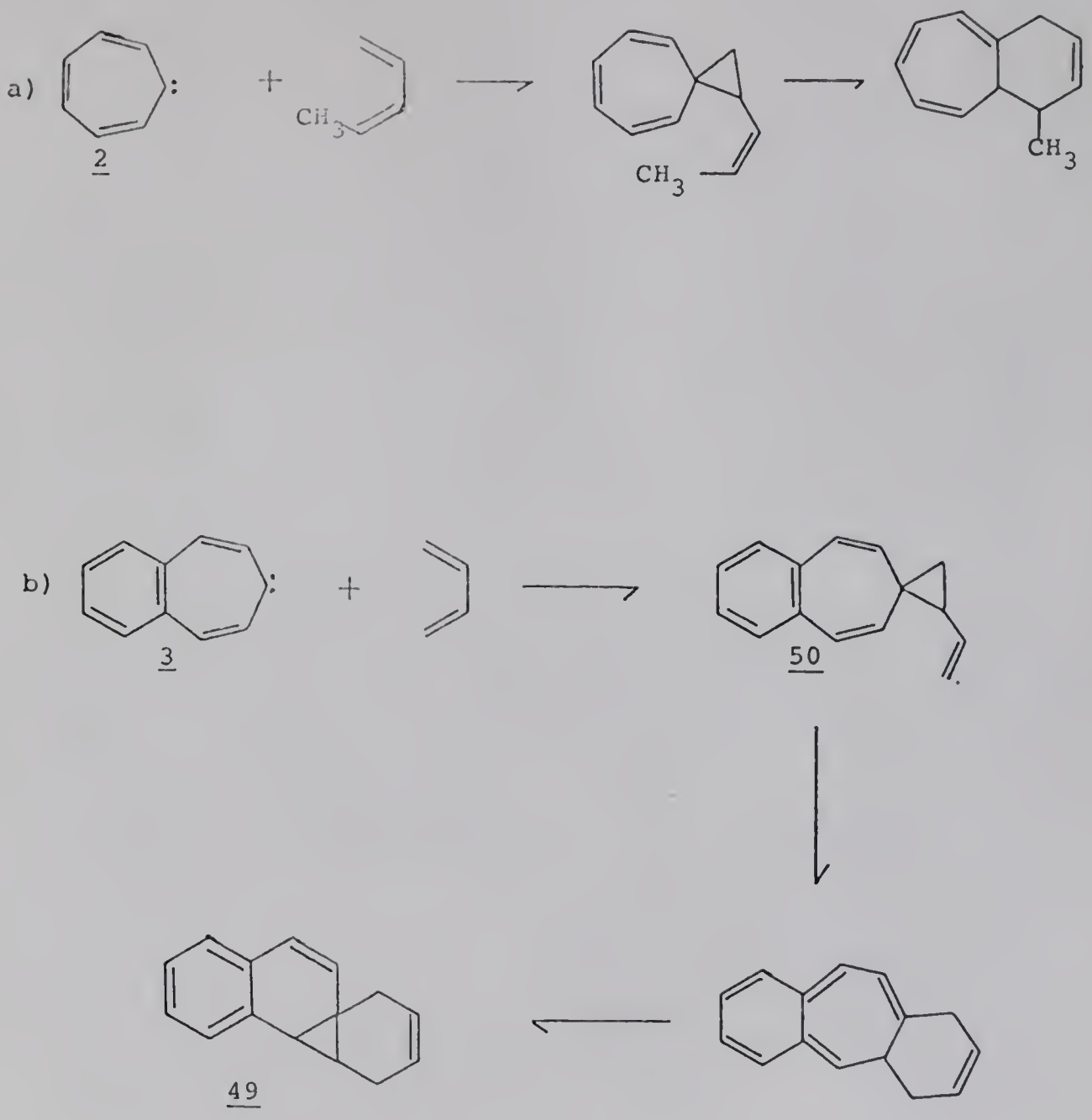
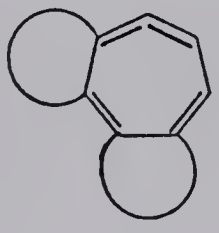
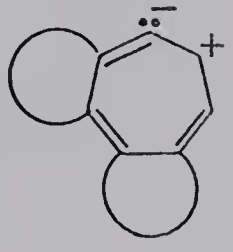


Figure 9

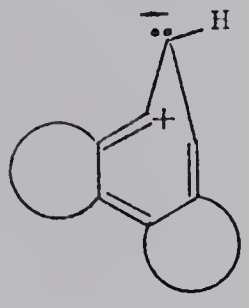
The lower adduct yield that results when 4,5-benzocycloheptatrienylidene (3) reacts with cyclopentadiene than when dibenzo[*a*,*e*]cycloheptatrienylidene (32) reacts with this diene (i.e., 16% yield from 3, 73% yield from 32) provides some assurance that an intermediate in which the annelated rings experience a decrease in resonance energy is not the reactive species. Thus it seems unlikely that a strained allene 51 or a zwitter ionic species (for example 52 or 6c) reacts with the diene. However, other more convincing arguments against some of these species have been offered previously.[1,2,10,48] Unfortunately, the low yields from 3



51



52



6

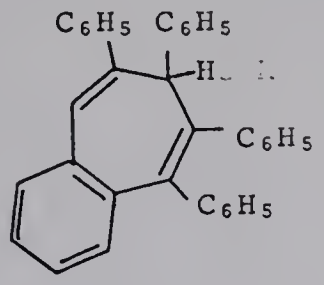
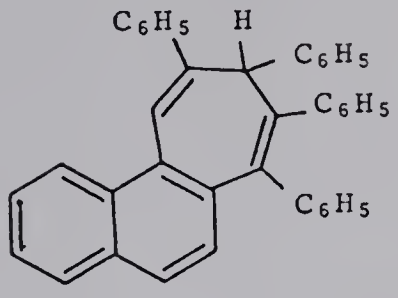
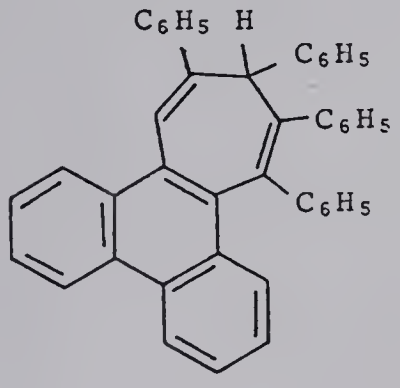
may be in no way related to the efficiency of cyclopropene trapping. A red-orange amorphous solid forms on photolysis of 4,5-benzotropone tosylhydrazone salt (53') and may possibly prevent complete photolysis of the salt by its more efficient light absorption. Typically, low yields result from photolytic generation of 4,5-benzocycloheptatrienylidene (3) regardless of the mode of reaction (i.e., trapping of the cyclopropene, trapping of the aromatic carbene, or trapping of the arylcarbene after rearrangement). Also, the requisite longer photolysis time may result in more extensive photorearrangement of initially formed adducts.

However, thermal generation of 4,5-benzocycloheptatrienylidene (3) (and hence the cyclopropene 5b) in the presence of tetracyclone clearly implies less efficient cyclopropene trapping than occurs in the analogous reaction of dibenzo[*a*,*c*]cycloheptatrienylidene 32 (and hence the cyclopropene 5c) with tetracyclone. Thermolysis (115° for 2 hours) of 4,5-benzotropone tosylhydrazone salt (53') in tetrahydrofuran containing tetracyclone yields a single $C_{39}H_{28}$ hydrocarbon product, 7,8,9,10-tetraphenyl-9*H*-cyclohepta[*a*]naphthalene (54) in 9% yield. The spectral properties of this product are as one would predict based on those of major hydrocarbene products resulting from reaction of other aromatic carbenes (i.e., 2[16] and 32) with tetracyclone (for example, the nmr chemical shift of the methine proton is as anticipated--see Table 6).

The major products from this reaction are apparently β-naphthylcarbene tetracyclone addition products, β-naphthyltetraphenylphenol (55) and 6a,11a-dihydro-7,8,9,10-tetraphenylbenzo[*a*]naphtho[2,3-*d*]furan (56). An analogous phenol is formed on addition of diazomethane to tetracyclone.[69] The spectral and chemical properties suggest that 55 is a polyarylphenol [ir: 3530 cm^{-1}, OH; nmr ($CDCl_3$) τ 4.78 (s, removed by shaking with D_2O); orange coloration in the presence of NaOH]. It has a molecular weight of 524 (mass spectrum) and the correct elemental analysis for a $C_{40}H_{28}O$ species. Only a tentative structure assignment is possible for 56. Spectral properties are consistent with the structure assigned, and the compound is certainly a $C_{40}H_{28}O$ compound

Table 6

Hydrocarbons from Reactions with Tetracyclone

Compound	^{1}H-nmr (τ) (methine proton)	Yield of Adduct
 10	4.63	25%
 54	4.57	9%
 46	4.52	50%*

*The isolated material is mainly an H-shift isomer with a trace of this material as an impurity.

(1:1, 3:tetracyclone), since the parent ion in the mass spectrum is found at m/e 524.

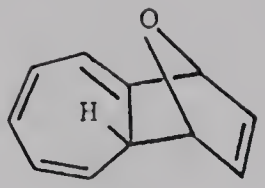
A lower yield of the typical cyclopropene adduct is expected if cyclopropene 5b is less stable (and hence is available in the reaction mixture for a shorter period of time) than cyclopropene intermediate 5c. Although other explanations for these results are possible, the hydrocarbon yields are completely consistent with the original expectation based on simple Huckel molecular orbital predictions[35] that 5b would be less stable than 5c. Similar reasoning rules out product formation from the less stable allene of 32. It is at least clear that none of the three compounds isolated (54, 55, or 56) is a precursor of any other. Neither thermolysis nor acid treatment converts any one product to any other.

Cycloheptatrienylidene (2) does not undergo rearrangement in solution so trapping of a rearrangement intermediate would not be expected. However, 2 does react with dienes to give products with the general structural features anticipated if they result from the cyclopropene intermediate 5a undergoing cycloaddition with the respective diene[10,48] (i.e., cycloheptatriene rather than norcaradiene isomers of adducts similar to 43, 44, 48, and 49). In other work (Chapter I) the reaction of cycloheptatrienylidene (2) with tetracyclone has been shown to be consistent with cyclopropene trapping but not necessarily requiring product formation by this mechanism.

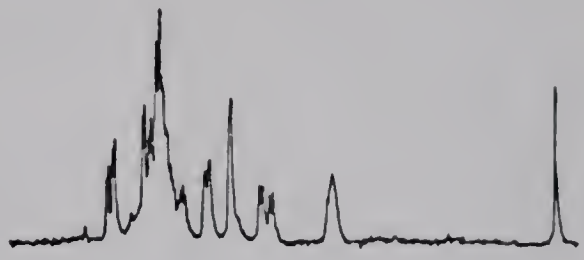
In one instance, reaction of the carbene 2 with *cis*-1,3-pentadiene, the adduct has been convincingly shown to not be the result of a Diels-Alder reaction of a cyclopropene intermediate (5a), but rather to be the final product of a two-step process as shown in Figure 9a (page 46). Since *cis*-1,3-pentadiene is an extraordinarily poor diene for a Diels-Alder trapping reaction, its reaction may not be representative of those of other dienes which react to give products consistent with trapping of the cyclopropene 5a and with no indication of isomeric adducts that rearrange to the observed product.

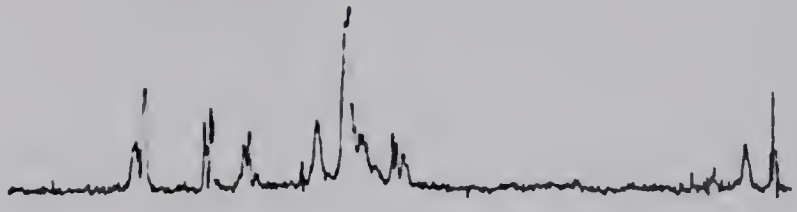
The possibility that the aromatic carbene 2 is in rapid equilibrium with the cyclopropene intermediate 5a in spite of the lack of further rearrangement to 1, seems worthy of experimental test. A clear differentiation is not possible employing most diene traps since (as outlined above) both the aromatic carbene 2 and the cyclopropene 5a react to eventually produce the same product. However, when cycloheptatrienylidene (2) is generated thermally in the presence of furan, the structure of the resultant adduct 57 suggests that cyclopropene trapping is not the mechanism of its formation. The isomer obtained is *exo*-1,4-epoxy-4*aH*-benzocycloheptene (57). The spectral properties are as expected from those of the other diene adducts. Lanthanide-induced proton nmr shifts leave little doubt that the *exo*-epoxy isomer is obtained. Spectra with increasing amounts of shift reagent present are shown in Figure 10. H4a is clearly situated

^{1}H-nmr Spectra of 57 with Increasing Amounts of Eu(fod)$_3$ Present



57





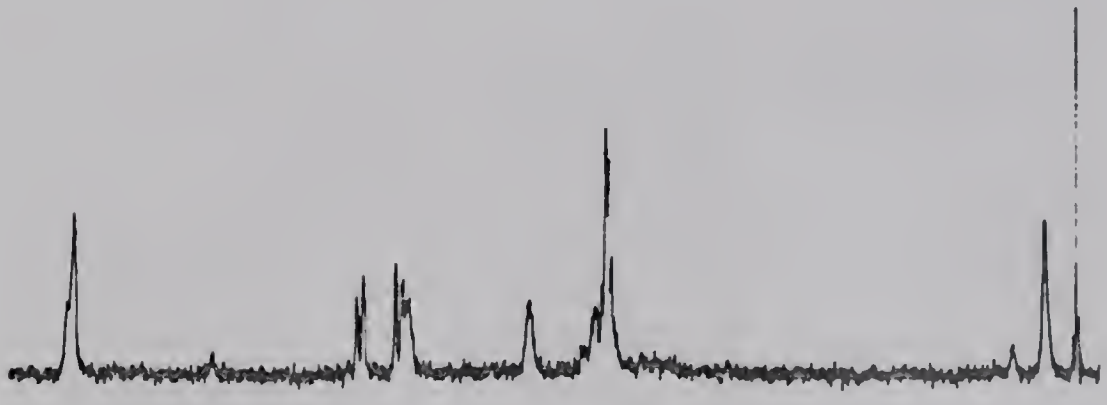


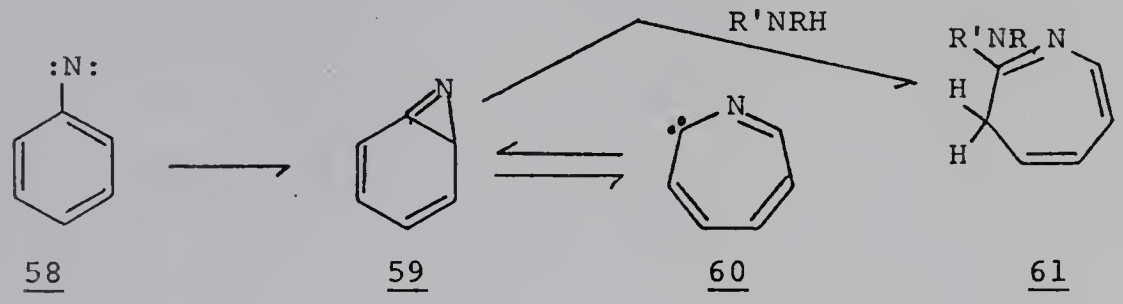
Figure 10

closer to the oxygen than the vinyl protons H2 and H3 by virtue of the greater induced nmr shift it undergoes on addition of $Eu(fod)_3$ (all angles being identical to $\pm 1^{o}$). A rough calculation (with the same assumptions as employed for the previous treatment of adduct 44) of agreement factors (*exo:* R=0.06; *endo:* R=0.16) confirms the *exo* geometry and amounts to a structure proof. Formation of this isomer, 57, by cycloaddition of the cyclopropene 5a to furan requires an *endo*-transition state. Since an *exo*-transition state is necessary in the reaction of dibenzo[*a*,*c*]cycloheptatrienylidene (32) (via the cyclopropene 5c) with furan to produce the observed adduct 44, and since there is strong evidence for a cyclopropene's participation in this reaction, it is unlikely that 57 results from cycloaddition of the cyclopropene 5a, and a two-step process is indicated. This is especially true since there seems to be no obvious alternative explanation for a reversal in mode of cycloaddition. Steric difference in 5a and 5c appear minor, and secondary orbital interactions[35,70] are similar (in fact, if favorable interaction between the oxygen orbitals of furan and the conjugated π-system of the cyclopropene accounts for *exo*-cycloaddition, 5a is more likely to react *exo* than 5c). However, since factors affecting the mode of furan cycloaddition are poorly understood, this experiment fails to offer more than tentative implication of a two-step reaction.

Due to the relatively small loss in resonance energy (Figure 4) accompanying isomerization, phenanthrylcarbene (33) might be capable of rearrangement to the cyclopropene intermediate 5c followed by cycloaddition with dienes. This intermediate 5c might well be generated even if further reorganization to the aromatic carbene 32 were not thermodynamically feasible. However, generation of 33 in the presence of furan fails to produce any trace of adduct 44 under either thermal (115°) or photolytic (-60°) conditions (limit of detection: 0.1%). Thus, an energetic ordering of the intermediates is precluded since one cannot ascertain whether thermodynamic or kinetic factors prevent detection of the cyclopropene intermediate 5c.

Cyclopropenes occasionally react with amines to produce cyclopropylamines,[71] but generally these reactions are sluggish, requiring a substantially polarized or highly electron deficient double bond.[15] The cyclopropene intermediate 5c would hardly be expected to undergo nucleophilic addition of amines. However, an intermediate such as 6c (or another dipolar species) should be quite susceptible to amine trapping. In view of the other evidence presented here, it is not surprising that no indication of addition was obtained when dibenzo[*a*,*c*]cycloheptatrienylidene 32 was generated in the presence of diethylamine. The product mixture was similar to that produced in the absence of trapping reagents or in the presence of ineffective traps.

Nucleophilic addition of amines is the strongest evidence implicating a 2*H*-azirine intermediate 59 in the rearrangement of phenylnitrene 58 to 2-azacycloheptatrienylidene 60.[72] The reaction of amines with azirines is expected to occur more readily than analogous reactions of amines



58 59 60 61

with cyclopropenes due to the greater polarity of the double bond, and amine addition to 2*H*-azirines has been experimentally demonstrated.[73] The extreme specificity for amines of the reactive intermediate resulting from phenylnitrene 58 is truly remarkable, particularly, since the presumably similar cyclopropene intermediate 5c is totally unreactive. Sundberg and coworkers have shown that 2-diethylamino-3*H*-azepine (61a, R,R'=Et) is best prepared with the amine present as a very dilute solution (about 2% in THF).[74] This report was confirmed on a preparative scale. In fact, a good yield of azepine 61b (R=*n*-butyl, R'=H) results from reaction of phenylnitrene (from photolysis of phenyl azide) with an equimolar amount of the amine. This is particularly remarkable since phenyl azide should be an equally effective trap for the preposed 2*H*-azirine intermediate 59.[75]

Furan also fails to react with the intermediate from phenylnitrene. This, too, is unexpected since 2*H*-azirines generally undergo 2+4 cycloaddition reactions with dienes only slightly less readily than do cyclopropenes. For example, the conditions for reaction of tetracyclone with 3-methyl-2-phenyl-1-azirine (3:4 molar ratio, refluxing toluene, 6 days, 65% yield[76]) are just slightly more vigorous than those for reaction of tetracyclone with 1,2,3-triphenylcyclopropene (1:1 molar ratio, refluxing benzene, 2 days, 75% yield[77]). Yet, with an equimolar quantity of amine as trap, the yield of 3*H*-azepine 61b is identical when furan is substituted for tetrahydrofuran as the reaction solvent. As mentioned previously, there is also no evidence that phenyl azide cycloaddition with the intermediate occurs, and a highly strained azirine such as 59 should be particularly susceptible to cycloaddition with phenyl azide.[75] In all, the evidence for azirine 59 as an intermediate in phenylnitrene rearrangements is decidely weak. The Wolff intermediate 62 seems equally satisfactory. However, attempted trapping experiments with dienes which are more susceptible to rapid reaction with 2*H*-azirines would be of interest.

62

An argument based on relative π-bond order of the reacting bond led to the correct choice of a cyclopropene mechanism for carbene-carbene rearrangements and a similar analysis when applied to the reorganization of heterocyclic carbenes[3,4] and nitrenes[14] strongly suggests a Wolff mechanism for these rearrangements (via an intermediate or transition state similar to 6 or 62). An evaluation of substituent effects on the direction of nitrene rearrangement from studies of arylnitrenes (particularly *ortho*-substituted phenylnitrenes[78]) suggests that nitrene reorganizations occur by a Wolff mechanism since the least stable 2*H*-azirine is often required to produce the observed product. However, such an analysis is not without question, and in fact the bond of highest π-bond order does migrate in arylnitrene rearrangements just as it does in carbene rearrangements, suggesting a 2*H*-azirine intermediate. The results reported here offer little evidence that would permit a mechanistic distinction. Clearly other factors which may influence the rearrangement require evaluation (intermediate energetics,[4] singlet-triplet crossing, prior azide-trap association, and possible simultaneous nitrogen loss with reorganization influenced by azide conformation,[78,79] for example). Naphthyl azide may fail to rearrange[80] since a Wolff mechanism leads to the very high energy intermediate, 3,4-benzoazacycloheptatrienylidene (analogous to 8), or it may fail to rearrange for reasons similar to those that prevent the rearrangement of naphthylcarbene (4) via a cyclopropene intermediate 5b

(yet, phenylnitrene 58 rearranges in solution, although phenylcarbene 1 does not.[1]). While a cyclopropene 5 is clearly implicated in rearrangement of carbenes into and out of carbocyclic systems, the older and better studied aryl-nitrene rearrangement still requires mechanistic evaluation.

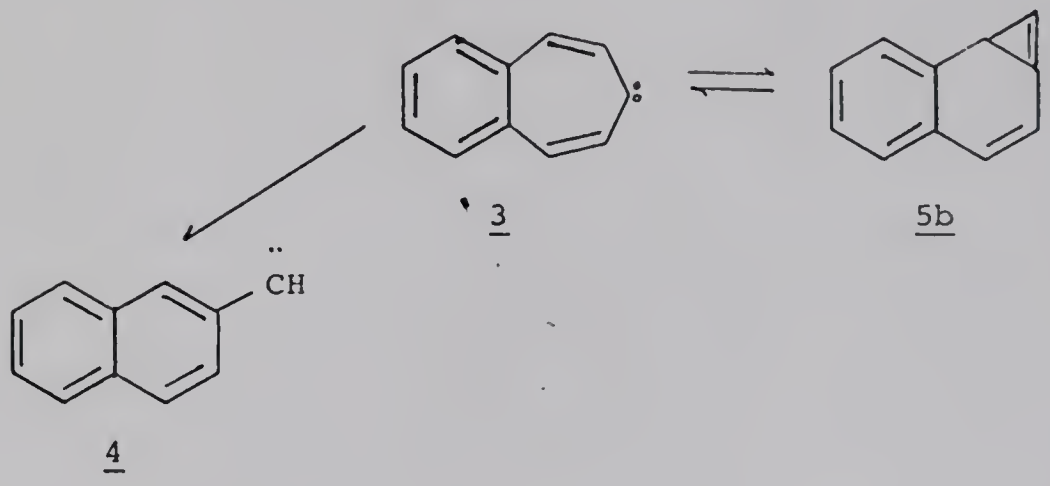
CONCLUSION

A concerted rearrangement via a cyclopropene-like transition state is unambiguously ruled out as a mechanistic possibility for carbene-carbene rearrangements occuring in solution. The evidence presented leaves little doubt that fused cyclopropene intermediates are generated from dibenzo[*a*,*c*]-cycloheptatrienylidene (32) and 4,5-benzocycloheptatrienylidene (3). That the cyclopropenes 5b and 5c are thus intermediates along the rearrangement pathway is implied.

However, other alternatives must also be considered. It is clear that irreversible cyclopropene formation and irreversible rearrangement cannot be competitive modes of destruction available to these aromatic carbenes. When formed by thermolysis at 120±10°, dibenzo[*a*,*c*]cycloheptatrienylidene (32) rearranges and is trapped in 95% yield as the benzene addition product 42 of phenanthylcarbene. This permits no more than 5% irreversible formation of cyclopropene 5c. However, under similar (120±10°) thermolysis conditions, the Diels-Alder adduct 46 of cyclopropene 5c and tetracyclone is isolated in 50% yield. Consequently, the suggestion that competitive, irreversible cyclopropene formation occurs and does not lead to the arylcarbene is refuted. Evidence based on a previous study of β-naphthylcarbene (4)

formation from 4,5-benzocycloheptatrienylidene (3), along with the tetracyclone trapping reported here leads to a similar conclusion in the case of carbene 3.

A more serious difficulty is the possibility that the aromatic carbenes 3 and 32 are in rapid equilibrium with the cyclopropenes 5b and 5c, respectively, with rearrangement occuring from the aromatic carbenes rather than the cyclopropenes. This is essentially the same problem that pre-



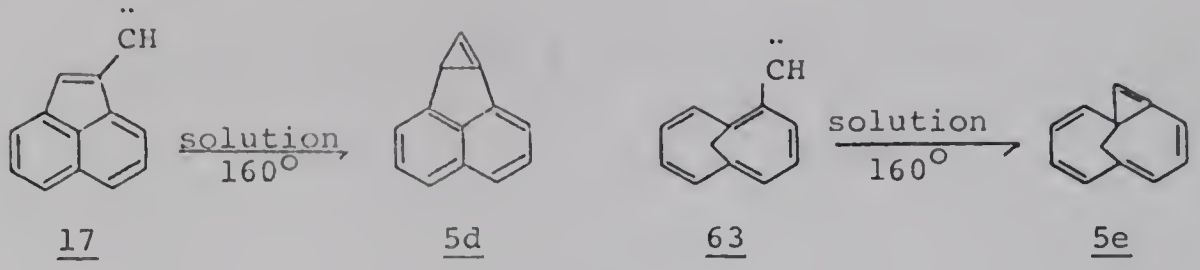
3 5b 4

vented a determination of whether the 7*H*-benzocycloheptenes 9 and 10 isolated from cycloheptatrienylidene 2 addition to tetracyclone resulted from reaction of the aromatic carbene 2 or the fused cyclopropene 5a (Chapter I). When there are a number of rapidly equilibrating intermediates, it is often difficult to state with certainty which intermediate produces the observed product. In general, unless structures of the final products provide convincing evidence, it is seldom possible to deduce from what point equilibrating intermediates convert to products.

The photochemical Wolff Rearrangement is a pertinent example. Although an oxirene intermediate (or transition state) is formed, it does not produce the rearranged products.[81] Oxirenes in carbonylcarbene rearrangements may offer a very close analogy to cyclopropenes in aromatic carbene rearrangements. Both may be side species not involved in the rearrangement.

However, some reasons for rejecting this possibility can be offered. In the first place, conclusive evidence that cyclopropene trapping occurs has only been obtained in the case of those carbenes (i.e., 3 and 32) that rearrange in solution. Evidence for cyclopropene trapping from cycloheptatrienylidene 2 (which does not rearrange in solution) is lacking. Secondly, all arylcarbenes and aromatic carbenes that have been observed to rearrange either in solution or in the gas phase,[1-10] rearrange predominantly, if not exclusively, via the more stable of the two possible cyclopropene intermediates (if two different intermediates are possible). Thus the direction of rearrangement can be predicted from stabilities of the intermediate cyclopropenes. This, in substance, is equivalent to the statement that addition to the bond of highest π-bond order occurs. Finally, the minimum conditions necessary for carbene-carbene rearrangements are determined by structural feature associated with the cyclopropene, insofar as the stability of the cyclopropene reflects the stability of the transition state for the rearrangements. 1-Acenaphthylcarbene (17) fails to rearrange in solution (due, presumably,

to the highly strained cyclopropene intermediate 5d necessary) while methano-10π-annulenylcarbene 63 (having a less strained cyclopropene intermediate 5e) rearranges readily.



17 5d 63 5e

Similarly, 4,5-benzocycloheptatrienylidene 3 rearranges rapidly in solution (due, presumably, to the lesser loss in resonance energy associated with formation of the cyclopropene intermediate 5b) while cycloheptatrienylidene 2 fails to rearrange in solution (since it loses much more resonance energy on formation of 5a). Therefore rearrangement via a

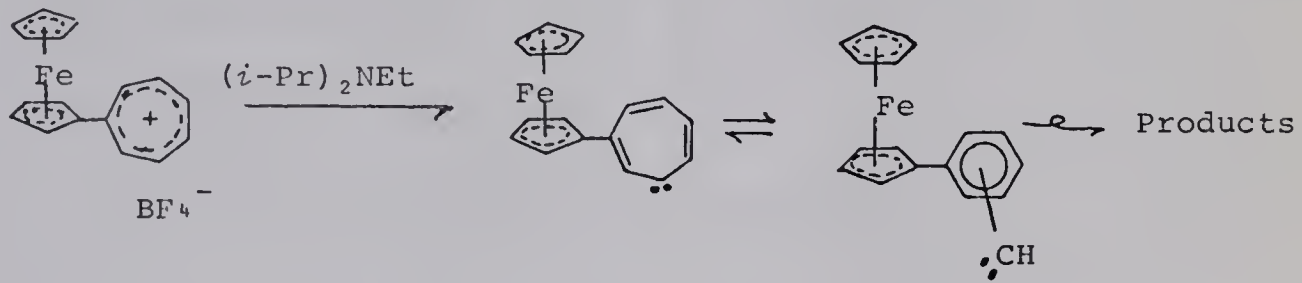
2 5a 3 5b

cyclopropene intermediate 5 seems likely, if not certain, and may be accepted in the absence of evidence to the contrary.

It may well be the case that the aromatic carbene, the cyclopropene, and the arylcarbene form successively and irreversibly. It has been experimentally demonstrated that arylcarbene 33 does not reversibly form the cyclopropene 5c. An alternative synthesis of the cyclopropene (best, 5b) and a

search for spiro-adducts due to the aromatic carbene (3) are required as an empirical test of equilibration of 3 and 5b. If the aromatic carbene is not formed from the cyclopropene precursor, the mechanistic sequence of intermediates in carbene-carbene rearrangements would be unequivocally established. However, this experiment remains to be carried out, and its results are not readily predictable, even if the mechanistic sequence for rearrangement is as proposed. In the gas phase, the reversibility of this rearrangement has been previously demonstrated.[1,6-10]

Since cyclopropene trapping is very characteristic of carbenes that rearrange in solution, it offers a method of establishing if observed rearrangements are actually carbene-carbene rearrangements. For example, attempted cyclopropene trapping might allow proof of the mechanism of product formation on treatment of ferrocenyltropylium fluoroborate with base which has been suggested to involve a carbene-carbene rearrangement.[82] Similarly, cyclopropene intermediate 5e



in the methano-10π-annulenylcarbene rearrangement[5] might be sought.

Initial efforts along this line, experimental tests to detect a 2*H*-azirine intermediate 59 in arylnitrene

rearrangements, proved futile. This suggests that an alternative mechanism pertains in this rearrangement. However, this one piece of negative evidence is insufficient to allow any definite conclusion. Yet the mechanism of arylnitrene rearrangements should not be assumed (as they often have[3,4,7]) to be analogous to the carbon analogue. The intermediacy of an oftpostulated[72,74,78,80] 2*H*-azirine intermediate 59 in the rearrangement remains open to question. Generation of phenylnitrene in the presence of more reactive dienes will be of interest.

EXPERIMENTAL

General.--Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Accurate mass measurements were provided by the High Resolution Mass Spectrometry Laboratory, Florida State University, Tallahassee, Florida. Ultraviolet and visible spectra were recorded on a Cary 15 double-beam spectrophotometer using 1-cm silica cells. Infrared spectra were recorded with a Beckman IR-10 spectrophotometer. In all cases where the KBr pellet technique was not used, sodium chloride plates were substituted. Nuclear magnetic resonance spectra were determined on a Varian A-60A high resolution spectrometer. A Varian XL-100 spectrometer was used for double resonance experiments and for some studies with Lanthanide shift reagents. Chemical shifts are reported in tau (τ) values from internal tetramethylsilane standard. Low resolution mass spectra were determined on a Hitachi model RMU-6E mass spectrometer.

Analytical thin-layer chromatography (tlc) was accomplished on 2 in. x 8 in. plates coated in these laboratories with 0.25 mm layers of E. Merck HF-254 silica gel; preparative work was conducted on 8 in. x 8 in. plates coated with 1.0 mm layers of HP-254 silica gel. Components were

visualized by their quenching of fluorescence under uv light. Analytical gas-liquid chromatography was accomplished with a Varian Aerograph Series 1200 flame ionization instrument using a 10' x 1/8" or a 5' x 1/8" column of 5% SE-30 on Chromosorb W AW DMSC. Analytical results were obtained by cutting and weighing Xerox copies of the chromatograms. Preparative gas-liquid chromatography was carried out on a Varian Aerograph 90-P thermal conductivity instrument using a 18' x 1/4" column of 20% SE-30 on Chromosorb W. MCB grade G2 silica gel or activity grade III Woelm basic alumina was used for column chromatography.

All chemicals are reagent grade used as supplied unless otherwise stated. Dioxane and tetrahydrofuran were dried by distillation from lithium aluminum hydride and passage over activity grade I Woelm basic alumina with subsequent storage over calcium hydride under a nitrogen atmosphere. 1,3-Cyclopentadiene was prepared in the standard way[83] from dicyclopentadiene previously dried over magnesium sulfate or 4A molecular seive. It was stored at Dry ice temperature over sodium sulfate under nitrogen and used within two weeks. Practical grade furan was washed with 5% sodium hydroxide, dried over calcium sulfate, distilled from KOH, passed through basic alumina (Woelm, Grade I), and stored under nitrogen. Diethylamine and butylamine were distilled from lithium aluminum hydride or sodium hydroxide and passed through a short grade I Woelm basic alumina column.

Acenaphthylene-1-carboxaldehyde (20).--The procedure was a modification of that described by Buu-Hoi and Lavit.[26] Acenaphthylene (20.0 g, 130.mmol, freshly sublimed), 15 ml toluene, and dimethylformamide (14.5 g, 200 mmol, dried over 4-A sieve) were mixed under nitrogen. A portion of the toluene (ca. 5 ml) was distilled to azeotrope away any water present. The distillation head was replaced with a reflux condenser having a nitrogen T and drying tube at the top. The flask was placed in a water bath at room temperature. While stirring vigorously with a large blade stirring paddle, phosphorous oxychloride (28.0 g, 182 mmol) was added dropwise over a five-minute period. The solution was warmed to 90° and stirred at this temperature for 20 minutes as the mixture darkened and partially solidified and then thinned to a dark oil. The crude products were cooled in an ice bath, and 20 ml saturated sodium acetate added very slowly. After filtration through Celite^{R} 545, the reaction mixture was extracted twice with dilute hydrochloric acid and twice with water. The very black organic solution was dried over calcium sulfate (anhydrous) and solvent removed. Volatile products were collected by vacuum transfer of all material distilling below 180° at 0.1 mm of Hg. Careful fractional distillation gave unreacted acenaphthylene (78-84°, 0.1 mm of Hg) followed by the desired product 20 (122-126°, 0.1 mm of Hg) as a stable yellow solid contaminated with about 6% acenaphthylene. Recrystallization from methylene chloride-pentane gave analytically pure acenaphthylene-1-carboxaldehyde (20) (5.7 g, 32 mmol, 24% yield)

with the following properties: mp 55.5-57°; ir (KBr): 3050, 2820, 1665, 1505, 1480, 1425, 1325, 1150, 1135, 975, 860, 770 cm^{-1}; ^1H-nmr (CCl_4): τ -0.05 (s, 1H), 1.79 (d, 1H), 2.1-2.75 (m, 6H); mass spectrum: m/e 180 (M^+).

Anal. Calcd. for $C_{13}H_8O$: C, 86.65; H, 4.47. Found: C, 86.50; H, 4.57.

The aldehyde 20 formed a semicarbazone in ethanol which after two recrystallizations from ethanol had mp 241-243° (with decomposition, somewhat dependent on the rate of heating), Lit.,[26] 240°, and under vacuum, mp 255-257°, Lit.,[26] 275°.

The aldehyde 20 (0.1 g, 0.6 mmol) was oxidized with chromic anhydride (0.25 g, 2.5 mmol) by refluxing 15 minutes in 10 ml glacial acetic acid. Workup as described[26] yielded a small amount of material that was converted to 1,8-naphthanoic anhydride (0.02 g, 0.1 mmol, 20% yield) by acetic anhydride. The crude final product was comparable by ir (ir (KBr): 3060, 1770, 1735, 1580, 1305, 1015, 775 cm^{-1}) to a commercial sample (Aldrich).

7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (34).--A modified procedure of Joshi, Singh, and Pande was employed.[40] Cetrimide^R (Pfaltz and Bauer, Inc.) was used as the cationic detergent (0.7 Cetrimide^R to 100 g phenanthrene) and the reaction was run to completion by stirring 15 hours at room temperature. Prior to recrystallization the product was decolorized by eluting rapidly through a large silica gel column with carbon tetrachloride. 34 obtained (89.9 g, 58% yield) was identical in all respects to that previously

characterized: mp 144-145°, lit. 140.2°[84] and 141.2°[40] (melting occurs with decomposition and is a function of the rate of heating).

6-Chloro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-ol (35).--7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (34) (5.85 g, 22.4 mmol) was thermolyzed under nitrogen at 170±5° in an oil bath for thirty minutes. The resultant oil was taken up in 100 ml of acetonitrile, and 130 ml of saturated sodium bicarbonate solution was added. The two-phase reaction mixture was stirred rapidly at room temperature for one hour as a salt precipitated. After dilution with 100 ml of water, the solution was extracted with three 75 ml portions of methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. Solvent was removed to yield 5.46 g (22.4 mmol, quantitative) of alcohol 35 suitable for further use.

Sublimation (150°, 0.15 mm of Hg) followed by grinding under pentane gave colorless crystals of analytical purity: mp 80.5-81.5°; uv: λ_{max} (C_2H_5OH), 239 nm (ε 41,000); ir (melt): 3420, 3060, 1625, 1480, 1085, 755, 730 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.3-2.9 (m, 8H), 3.31 (s, 1H), 4.12 (d, J=6 Hz, 1H), 7.26 (d, J=6 Hz, 1H); mass spectrum: m/e 242 (M^+).

Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.68; Cl, 14.60. Found: C, 74.35; H, 4.71; Cl, 14.75.

6-Chloro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (36).--Activated manganese dioxide (Winthrop Laboratories, 30.0 g, 330 mmol) and 6-chloro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-ol (35) (5.27 g, 21.8 mmol) were stirred in 200 ml methylene chloride at room temperature under nitrogen for one hour. Anhydrous calcium sulfate was added, and the mixture was suction filtered through Celite 545^{R}. The residue was washed thoroughly with 500 ml of ethyl acetate. Solvent was removed and the oil column chromatographed on silica gel with carbon tetrachloride-methylene chloride (4:1). The crystalline product (36) obtained after solvent removal (4.69 g, 19.5 mmol, 90% yield) was suitable for further use.

Recrystallization from benzene-heptane gave analytically pure 36: mp 98.0-98.8°, lit.[41,42] 95.5-97.0° and 98°; ir (KBr): 1665, 1605, 1595 cm^{-1}, lit.[41,42] 1665, 1610, 1595 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.0-2.7 (m); mass spectrum: m/e 240 (M^+). On contact with the face, 36 is an annoying skin irritant.

6-Chloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (37).--Catalytic hydrogenation of 6-chloro-5*H*-dibenzo[*a*,*c*]-cyclohepten-5-one (36) (4.59 g, 19.1 mmol) was carried out over 5% palladium on carbon (0.75 g) in 75 ml ethyl acetate containing one milliliter of glacial acetic acid using a standard atmospheric pressure hydrogenation apparatus.[85] Hydrogen (468 ml, uncorrected for solvent vapor) was taken up in 3.4 hours at one atmosphere pressure and 24°. The reaction mixture was filtered through sodium carbonate (anhydrous), washed with ethyl acetate, and solvent removed.

The crude product mixture consisted of 20% unreacted starting material 36, 67% desired product 37, and 13% of a product formed on further hydrogenolysis, 6,7-dihydro-5*H*-dibenzo-[*a*,*e*]cyclohepten-5-one (39). The desired product 37 contaminated with 16% starting material (3.57 g) eluted as the first major component from a silica gel column with carbon tetrachloride. Recrystallization from ethanol-water yielded 37 (3.08 g, 12.7 mmol, 76% yield), and a portion of starting material was recovered (0.52 g).

Analytically pure 37 was obtained after a second recrystallization from ethanol-water: mp 89-90°; uv: λ_{max} (C_2H_5OH), 305 nm (ε 1,600), 238 (24,000); ir (KBr): 3060, 3020, 2920, 1695, 1595, 1205, 920, 800, 795, 655 cm^{-1}; ^{1}H-nmr (benzene-d_6): τ 2.3-2.6 (m, 2H), 2.7-3.2 (m, 6H), 4.62 (t, J=7.5 Hz, 1H), 7.05 (d, J=7.5 Hz, 2H); ^{1}H-nmr (acetone-d_6): τ 2.1-2.7 (m, 8H), 4.11 and 7.03-6.29 (ABX pattern, ν_A = τ 6.81, ν_B = τ 6.48, ν_X = τ 4.11, J_{AB} = 13.5 Hz, J_{AX} = 9.0 Hz, J_{BX} = 4.5 Hz, 3H); ^{1}H-nmr (CCl_4): τ 2.3-2.9 (m, 8H), 4.52 and 6.6-7.1 (unusual ABX pattern, ν_A = τ 6.84, ν_B = τ 6.61, ν_X = τ 4.52, J_{AB} = 13.5 Hz, J_{AX} = 12. Hz, J_{BX} = 3. Hz, 3H); mass spectrum: m/e 242 (M^+), 180 (M^+ - COCl, major peak).

Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.68; Cl, 14.60. Found: C, 74.02; H, 4.73; Cl, 14.53.

6,7-Dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (39).--

a) This material was eluted as the second major component off the silica gel column with carbon tetrachloride containing increasing amounts of methylene chloride as eluent. 39 (0.33 g, 1.6 mmol, 10% yield) was obtained after recrystallization from methanol-water. Sublimation gave analytically pure material: mp 85.0-85.8°, lit.[43] 85-86°.

b) 6-Chloro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (36) (0.175 g, 0.729 mmol) was catalytically reduced on 5% palladium on charcoal (0.034 g) in 12 ml absolute ethanol containing anhydrous sodium acetate (0.150 g, 1.83 mmol). Two equivalents of hydrogen (35.7 ml at one atmosphere and 24°) were taken up in 40 minutes at which point hydrogenation ceased. The reaction mixture was filtered, and solvent removed. Sublimation (80°, 0.15 mm of Hg) gave analytically pure 39 (0.144 g, 0.547 mmol, 82% yield) identical to that obtained by procedure a): mp 85-86°, lit.[43] 85-86°; ir (melt): 3060, 2930, 1675, 1595, 1445, 1265, 750 cm^{-1}, lit.[43] $\nu_{C=O}$ 1678 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.2-2.8 (m, 8H), 7.00 (s, 4H); ^{1}H-nmr (benzene-d_6): τ 2.05-2.3 (m, 1H), 2.7-3.2 (m, 7H), 7.2-7.7 (m with AA'BB' pattern, 4H); mass spectrum: m/e 208 (M^+), 207 (major peak), 180 (M^+-CO).

Mixtures of 6-Chloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (37) and 6,7-Dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (39) from Catalytic Reduction.--6-Chloro-5*H*-dibenzo-[*a*,*c*]cyclohepten-5-one (36) (0.112 g, 0.47 mmol) and 0.05 g of 5% Pd on carbon were placed in 10 ml of solvent and hydrogenated until 11.4 ml of the hydrogen (0.51 mmol) had been taken up. The reaction products were worked up as before (filtration and solvent removal), and the ratio of chloroketone 37 to ketone 39 determined by nmr. The following results were obtained:

Solvent	Mole Ratio 37/39	Reduction Time (minutes)
Ethanol	0.3	7
Ethyl acetate (1% HOAc)	5.2	35
HOAc (glacial)	3.0	20
1:1 Benzene/cyclohexane	0.9	70
Methyl propionate	3.5	40

5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one (38).--To a solution of anhydrous lithium chloride (13.0 g, 400 mmol) in 200 ml dimethylformamide (dried over 4A sieve) was added 6-chloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (37) (3.03 g, 12.5 mmol), and the solution was stirred at reflux under nitrogen for fifteen hours. The solvent was distilled off until lithium chloride began to precipitate. The pot residue was diluted with 300 ml of water and extracted with three 40 ml portions of methylene chloride. The organic extracts

were combined and dried over anhydrous magnesium sulfate. Filtration and solvent removal left a viscous oil from which the last bit of dimethylformamide was removed *in vacuo*. The oil was column chromatographed on silica gel with carbon tetrachloride containing increasing amounts of chloroform. Crystalline 38 was obtained after solvent removal (2.20 g, 10.7 mmol, 85% yield). Sublimation (120°, 0.2 mm of Hg) gave white crystals (1.93 g) with the following properties: mp 83-84.5°, lit.[38] 83-85°; ir (KBr): 3060, 3030, 1640, 1590, 1405, 1295, 790, 785, 770, 755, 740, 730, 570 cm^{-1} (identical to a published spectrum[86]); ^{1}H-nmr ($CDCl_3$): τ 1.9-2.8 (m, 9H), 3.35 (d, J=12 Hz, 1H); mass spectrum: m/e 206 (M^+), 178 (M^+-CO, major peak).

Preparation of Tosylhydrazones.--Benzaldehyde free tropone was prepared by the hydrolysis procedure of Harmon and Coburn[87] and converted to the tosylhydrazone as previously described.[47] 4,5-Benzotropone tosylhydrazone (53) was synthesized in the reported manner,[1] as were phenalen-1-one tosylhydrazone (19) and the analogous benzenesulfonylhydrazone of phenalen-1-one.[25] New tosylhydrazones were prepared in the conventional way by stirring equal molar quantities of tosylhydrazide and the aldehyde of ketone in absolute ethanol (1 g/30 ml) with a drop of concentrated sulfuric acid for 15 to 20 hours.[1] The following products were obtained after recrystallization from ethanol: 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone (41), 94%

yield; mp 192-195° (with decomp.); ir (KBr): 3205, 3060, 1631, 1595, 1170, 1082, 760, 740, 670, 610 cm^{-1}; ^{1}H-nmr (DMSO-d_6): τ 0.39 (bs, 1H), 2.1-2.8 (m, 12H), 2.85-3.4 (d of doublets, 2H), 7.67 (s, 3H); mass spectrum: m/e 374 (M^+), 190 (major peak); Anal. Calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.57; H, 4.85; N, 7.48; Found: C, 70.42; H, 4.96; N, 7.25; Phenanthrene-9-carboxaldehyde tosylhydrazone (45), 95% yield; mp 161-167° (with decomp.); ir (KBr): 3190, 3070, 1640, 1600, 1500, 1455, 1170, 935, 755, 580 cm^{-1}; ^{1}H-nmr (DMSO-d_6): τ -1.7 (bs, 1H), 1.0-1.5 (m, 4H), 1.8-2.7 (m, 10H), 7.67 (s, 3H); mass spectrum: m/e 374 (M^+), 190 (major peak); Anal. Calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.57; H, 4.85; N, 7.48; Found: C, 70.66; H, 4.90; N, 7.40; Acenaphthylene-1-carboxaldehyde tosylhydrazone (21), 95% yield; mp 158-159°; ir (KBr): 3190, 3060, 1595, 1425, 1350, 1305, 1165, 1050, 915, 810, 775, 665, 600, 560, 545, 530 cm^{-1}; ^{1}H-nmr (acetone-d_6): τ -0.18 (bs, 1H), 1.64 (d of doublets, 1H), 1.78 (s, 1H); 1.95-2.8 (m, 10H), 7.70 (s, 3H); mass spectrum: m/e 164 (major peak); Anal. Calcd. for $C_{20}H_{16}N_2O_2S$: C, 68.95; H, 4.63; N, 8.04; Found: C, 69.00; H, 4.72; N, 8.08.

Preparation of Sodium Salts of Tosylhydrazones.--The sodium salts were prepared in the dry box under a nitrogen atmosphere, by dissolving the tosylhydrazone in dry tetrahydrofuran (ca. 2 g/50 ml) and adding 1.1 equivalents of sodium hydride (57% in mineral oil; Alfa Inorganics) slowly with stirring. Stirring was continued for an additional one hour. An equal volume of spectrograde pentane was added, and the resulting precipitate filtered, dried under vacuum,

and stored in a dark bottle in the dry box. The preparation was assumed to be quantitative and further reactions are based on weight of tosylhydrazone consumed.

Thermolysis and Photolysis of Aldehyde and Ketone Tosylhydrazone Sodium Salts.--Thermolyses were carried out in a sealed tube (a 3 oz or 1 oz Fisher-Porter Aerosol Compatibility Tube) containing a magnetic stirring bar. The tube was well flushed with nitrogen and charged in the dry box. The thermolysis temperature was maintained within $\pm 5^{\circ}$ in a preheated silicone oil bath. After cooling to room temperature the tube was vented to a gas buret that permitted a determination of nitrogen evolution. "Hot tube" pyrolyses for gas phase generation of carbenes were performed with a Pyrex^{R} apparatus modeled after that employed for phenylcarbene-cycloheptatrienylidene generation.[1] A hot zone 16 cm in length was maintained at the desired temperature ($\pm 20^{\circ}$) with a Chrome^{R} resistance wire (22 gauge) controlled with a variac. The tube was evacuated with an Edwards High Vacuum, Inc., model ES 330 high vacuum pump with a displacement of 11.8 CFM. A nitrogen flow measured at atmospheric pressure was maintained during addition to give a pressure of 1 to 2 mm of Hg. Dry firebrick (dried under high vacuum at 250° overnight) was used as an inert support and diluent for the anhydrous salts. The firebrick was retained in the tube by a glasswool mat located about 2/3 of the way down the hot zone. A salt was added from a solid addition tube (charged in the dry box) over a half-hour period, and products were

condensed in a trap immersed in liquid nitrogen. For small scale photolyses (0.1-0.4 g), an apparatus having two Pyrex tubes sealed into a small volume cooling jacket 3 cm apart was employed. A 550 W Hanovia "High-Pressure Quartz Mercury-Vapor Lamp" was placed in one tube, and the other tube of 35 ml maximum volume was used as the reaction vessel. An electronic stirrer was inserted through one of two ground glass inlets to the reaction vessel. A nitrogen atmosphere was maintained via the other inlet. For room temperature photolyses, the apparatus was immersed in a water bath and a tap water flow through the cooling jacket controlled the temperature at 30±5°. For low temperature photolyses, the apparatus was immersed in a Dry ice-methanol bath and methanol cooled with Dry ice was circulated through the cooling jacket by a magnetic drive centrifugal pump. The temperature was thus held at -60±5°.

Preparative-scale Photolysis of Diazo-2,3,4,5-tetraphenylcyclopentadiene in Benzene at 100°.--Diazo-2,3,4,5-tetraphenylcyclopentadiene[88] (0.50 g, 1.25 mmol) and 40 ml benzene (fresh bottle) were added to a 3 oz Fisher-Porter Aerosol Compatibility Tube in the dry box. The tube was sealed under nitrogen and heated in a boiling water bath (100±5°) with external photolysis (550 W Hanovia, Pyrex filter). Photolysis was discontinued after six hours at greater than 90% completion (tlc (benzene) showed a trace of the diazo starting material remaining). Solvent was removed

under reduced pressure and the principal product, 1,2,3,4,5-pentaphenylcyclopentadiene (16) (0.39 g, 0.88 mmol, 68% yield), isolated by crystallization from ethanol. Recrystallization from xylene gave 16 as a white solid with the following properties: mp 248-252°, lit.[17,22] 244-246°, 247°, 254°; ir (KBr): 3080, 3050, 3020, 1595, 1570, 1484, 1440, 1070, 1030, 910, 835, 785, 770, 755, 720, 695, 680, 550 cm^{-1} (identical to the published[22b] spectrum); uv: λ_{max}(cyclohexane) 340 nm (log ε 4.01), 268 (4.34), 245 (4.44), lit.[22b] λ_{max}(cyclohexane) 338-340 nm (log ε 4.00), 269 (4.35), 245 (4.44).

Small-scale Photolysis of Diazo-2,3,4,5-tetraphenylcyclopentadiene in Benzene at 100°.--Diazo-2,3,4,5-tetraphenylcyclopentadiene (0.035 g, 0.090 mmol) and 7.3 ml benzene were placed in a 1 oz compatibility tube and photolyzed (550 W Hanovia, Pyrex filter) 5 hours while heating in a boiling water bath (100±5°). The light path length was half that of the preparative photolysis, and the cell was half as wide and 3/4 as high, making the rate of photolytic rearrangement five times as great with an equivalent rate of thermal rearrangement. The photolysis went to completion, and on cooling three products were detected by tlc (cyclohexane/15% toluene) and glc (5% SE-30, 10' x 1/8", 235°), 1,2,3,4,5-pentaphenylcyclopentadiene (16) (R_t=47 min, identical to material previously prepared by glc (coinjection) and tlc), 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9)

(R_t=52 min, identical to authentic material supplied by T. Mitsuhashi), and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) (R_t=59 min, identical to Mitsuhashi's authentic material) in a mole ratio of 47:10:43.

Pyrolysis of Tropone Tosylhydrazone Sodium Salt in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone.--Tropone tosylhydrazone sodium salt (0.038 g, 0.128 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (0.10 g, 0.26 mmol) were dissolved in 11 ml benzene, placed in a 1 oz compatibility tube under nitrogen, and heated in a boiling water bath (100±5°) for five hours. Gas chromatography (5% SE-30, 10' x 1/8", 235°) showed, besides a substantial amount of unreacted 2,3,4,5-tetraphenylcyclopentadienone (R_t=37 min), the two 7 -benzocycloheptenes, 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) (identical by tlc (benzene) and glc with authentic samples supplied by T. Mitsuhashi), in a mole ratio of 0.20:0.80. No 1,2,3,4,5-pentaphenylcyclopentadiene (16) was detected.

Photolysis of 1,2,3,4-Tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-Tetraphenyl-7*H*-benzocycloheptene (10).--A dilute solution of 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) in 8 ml benzene was prepared from authentic samples supplied by T. Mitsuhashi. Gas chromatography (5% SE-30, 10' x 1/8", 235°) indicated a 1.85:1 molar ratio (9 to 10). The solution

was photolyzed (550 W Hanovia, Pyrex filter) 4 hours at 100±5° in a 1 oz compatibility tube, and again analyzed by gas chromatography. A molar ratio of 1.5:1 (9:10) with slight peak broadening was observed. Since the peaks overlap by about 20% on the chromatogram, the results are identical before and after photolysis within the experimental error. Thus the photolysis products are stable to the reaction conditions, and gas chromatography gives a good estimate of the amount of each isomer formed.

Room Temperature Photolysis of Diazo-2,3,4,5-tetraphenylcyclopentadiene in Benzene.--Diazo-2,3,4,5-tetraphenylcyclopentadiene (0.30 g, 0.75 mmol) was photolyzed (450 W Hanovia, Pyrex filter, low conversion) 1 hour in 250 ml benzene using a preparative reactor with a water-cooled Hanovia immersion well. Tlc (cyclohexane/15% toluene) and glc (5% SE-30, 10' x 1/8", 235°) comparisons with authentic samples (prepared by T. Mitsuhashi) demonstrated the presence of 1,2,3,4-tetraphenyl-7*H*-benzocycloheptene (9) and 5,6,7,8-tetraphenyl-7*H*-benzocycloheptene (10) in a 1:1 molar ratio. No 1,2,3,4,5-pentaphenylcyclopentadiene (16) could be detected.

Pyrolysis of Phenalen-1-one Tosylhydrazone Sodium Salt (19') in Dioxane.--Phenalen-1-one tosylhydrazone sodium salt (19') (0.29 g, 0.78 mmol) was weighed into a Fisher-Porter Compatibility Tube in the dry box under nitrogen and 40 ml dry dioxane added. The tube was placed in a preheated silicon oil bath, and the reaction mixture was stirred for

25 minutes at 160°. The mixture was cooled and a portion (2.5%) subjected to quantitative gas chromatography with anthracene (7.3×10^{-3} g) added as a standard. Phenalene (23) (0.0090 g, 0.054 mmol, 6.9% yield) was the only significant (>0.1%) volatile product detected by gas chromatography (5% SE-30, 10' x 1/8", 125°). This product had a retention time (R_t=15.7 min) identical to that of authentic material prepared according to Boekelheide and Larrabee.[28] Tlc (pentane or CCl_4) also indicated that the major product was identical to the authentic phenalene (23) with an nmr spectrum [^{1}H-nmr (CCl_4): τ 2.5-3.3 (m, 6H), 3.52 (d of t, 1H), 4.12 (d of t, 1H), 6.05 (bs, 2H)] as shown in the literature.[27] No trace of 1-methylacenaphthylene (26) or an acenaphthylcarbene dioxane insertion product 27 was noted in the chromatogram (limit of detection better than 0.01%). Another portion of the reaction mixture was evaporated to dryness at 60° under reduced pressure, taken up in benzene, and chromatographed (benzene) on a Woelm alumina column (Grade III). Phenalene (23) was separated at the solvent front followed by peropyrene (24) (9.4×10^{-4} g, 5.8×10^{-3} mmol, 0.75% yield) which was quantitated by uv-vis spectrophotometry in benzene. Due to its carcinogenic nature[31] no attempt was made to isolate pure peropyrene (24), but properties of dilute solutions left little doubt as to the identity of this hydrocarbon. The uv-vis spectrum was consistent with that reported: λ_{max} (benzene) 443, 416, 393, 373, 326 nm (log ε 5.20, 4.93, 4.56, 4.18, 4.87), lit.[29] λ_{max} 443.5,

415.5, 393, 371, 352, 326 nm (log ε 5.22, 4.90, 4.44, 3.98, 3.48, 4.77). Tlc (benzene or chlorobenzene) and glc (5% SE-30, 5' x 1/8", 300°, R_t=19 min) were identical to those of authentic 24 prepared by the method of Aoki.[30] A small amount of the trivial phenalen-1-one azine (22) was also isolated from the column as a very slow moving red band. The azine was identical (tlc, uv-vis, nmr) to authentic material prepared by the method of Hunig and Wolff.[25]

Pyrolysis of Acenaphthylene-1-carboxaldehyde Tosylhydrazone Sodium Salt (21') in Dioxane.--Acenaphthylene-1-carboxaldehyde tosylhydrazone sodium salt (21') (0.27 g, 0.73 mmol) in 40 ml dry dioxane was heated 20 minutes at 150° in a sealed tube under conditions similar to those employed for thermolysis of the ketone tosylhydrazone sodium salt 19'. The solution was cooled and nitrogen evolution measured: 10.3 ml (24°, 1.00 atm uncorrected for solvent vapor, ca. 57% yield). The substantial quantity of white solid present in the reaction mixture was filtered from the solution and dissolved in 100 ml chloroform. The chloroform solution was extracted three times with water to remove any sodium toluenesulfinate present. The solution was dried and solvent volume reduced until clouding occurred. The solid that crystallized from the solution at 0° was collected and recrystallized from chloroform. The compound was identified as the trivial diazocyclization product, 7*H*-acenaphtho[1,2-*c*]-pyrazole (25): mp 238-241°, lit.[32] 239°; ir (KBr): 3040,

2900, 1470, 1405, 1290, 1170, 1035, 980, 820, 770, 620 cm^{-1}; ^{1}H-nmr (DMSO-d_6): τ 1.9-2.4 (m). The soluble reaction products were quantitatively determined by gas chromatography with a weighed standard added and were isolated by preparative gas chromatography (20% SE-30, 18' x 1/4", 225°). 1-Methylacenaphthylene (26) (0.008 g, 0.05 mmol, 7%) was the major product (R_t=15 min) isolated and had properties consistent with those reported: ir (film): 3040, 2920, 2850, 1480, 1460, 1450, 1430, 840, 810, 770 cm^{-1}, lit.[33], 838, 805, 770 cm^{-1}; ^{1}H-nmr (CCl_4): τ 2.3-2.7 (m, 6H), 3.42 (bs, 1H), 7.63 (d, J=2 Hz, 3H), lit.[33], τ 7.65 and 7.63; mass spectrum: m/e 166 (M^+, 61), 165 (M^+-1, 100), lit.[33], 166 (52), 165 (100). The minor product (R_t=23 min) is tentatively identified as the dioxane insertion product 27 of acenaphthylcarbene (0.006 g, 0.024 mmol, 3% yield) from its nmr spectrum: ^{1}H-nmr (CCl_4): τ 2.2-2.65 (m, 6H), 3.30 (bs, 1H), 6.1-6.6 (m, 7H), 7.1-7.3 (ca. d, 2H). No evidence for any phenalene 23 or peropyrene 24 could be detected by gas chromatography with coinjection of authentic samples.

"Hot Tube" Pyrolysis of Phenalen-1-one Tosylhydrazone Sodium Salt (19').--Phenalen-1-one tosylhydrazone sodium salt (19') (0.46 g, 1.25 mmol), was gound in the dry box with approximately one gram of dry firebrick and placed in a solid addition tube with a nitrogen inlet. The salt 19' was dropped down the short pyrolysis tube at 410° in 1/2 hour. Products were condensed in a liquid nitrogen trap containing a glasswool pad to break aerosols. After warming

to room temperature under nitrogen, products were dissolved in 100.0 ml benzene (spectrograde) and quantitatively analyzed by gas chromatography (10' x 1/8", 5% SE-30, 160°) with *trans*-stilbene as a standard. Phenalene (23) (R_t=14 min, identical with authentic material[28] and that isolated previously as determined by coinjection, 1.1×10^{-3} g, 0.0065 mmol, 0.53% yield) was the major product, and 2,3-dihydrophenalene 28 (R_t=11 min, 8.5×10^{-5} g, $5. \times 10^{-4}$ mmol, 0.05% yield) was a minor product which was characterized by uv spectrophotometry (uv: λ_{max}(EtOH) 228 and 289 nm, qualitatively identical to the spectrum shown in the literature[28]). Five other components present in slightly lesser amounts were also indicated by gas chromatography. Glc at 300° on a 5-foot column showed peropyrene (24) as the major product from the pyrolysis. By uv-vis spectrophotometry (benzene) of the crude product mixture, peropyrene (24) (0.0078 g, 0.025 mmol, 3.8% yield) was also detected (identical by glc, tlc, and uv-vis with authentic material[30] and that isolated previously). No 1-methylacenaphthylene (26) was present to a limit of detection of 0.005% by gas chromatography with coinjection of product mixtures from pyrolyses of acenaphthylcarbene.

"Hot Tube" Pyrolysis of Phenalen-1-one Benzensulfonylhydrazone Sodium Salt.--The benzenesulfonylhydrazone sodium salt of phenalen-1-one (0.30 g, 0.84 mmol) ground with 1.2 g of dry firebrick was dropped down the hot tube at 360° in 40 minutes. The pyrolysis products were isolated from the

trap and dissolved in carbon tetrachloride. A qualitative comparison of the products with those obtained on pyrolysis of the tosylhydrazone salt of this ketone by gas chromatography at 160° indicated only two common products, phenalene (23) and 2,3-dihydrophenalene (28). The five minor unidentified components which are different in the two mixtures must result from the benzenesulfonyl or tosyl portion of the molecule. Coinjection of commercial samples suggested the nature of the two major compounds of these groups: the shortest retention time material was thiophenol (or thiocresol) and the longest retention time material was phenyl disulfide (or toly disulfide). Coinjection of the two crude product mixtures produced a new compound with a retention time intermediate between phenyl disulfide and toly disulfide (likely, the unsymmetrical disulfide), but only phenalene (23) and dihydrophenalene (28) superimposed on the chromatogram. Peropyrene (24) was also shown to be a common product by glc at 300°.

"Hot Tube" Pyrolysis of Acenaphthylene-1-carboxaldehyde Tosylhydrazone Sodium Salt (21').--Acenaphthylene-1-carboxaldehyde tosylhydrazone sodium salt (21') (0.45 g, 1.21 mmol), was pyrolyzed and products isolated and quantitated under conditions as nearly identical as possible to those employed for the hot tube pyrolysis of the ketone tosylhydrazone salt (19') (i.e., 410°, firebrick support, 1/2 hour addition, gas chromatography with stilbene as standard, and quantitative uv-vis spectrophotometry in benzene). Phenalene (23)

(0.0066 g, 0.040 mmol, 3.3% yield), 1-methylacenaphthylene (26) (0.0036 g, 0.022 mmol, 1.8% yield, identical by coinjection with material previously characterized), and toluenesulfinate reduction products as observed from pyrolysis of the aromatic carbene 19' were detected by gas chromatography at 160°. Peropyrene (24) (0.0105 g, 0.0322 mmol, 5.3% yield) was also present as shown by gas chromatography (300°) and uv-vis spectrophotometry.

9-(2,4,6-Cycloheptatrien-1-yl)phenanthrene (42).--a) 5*H*-Dibenzo[*a*,*e*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.16 g, 0.40 mmol) was heated with stirring in 35 ml of reagent grade benzene for 2 hours at 125° in a sealed tube. A quantitative evolution of nitrogen (9.7 ml at 24° and 1.00 atmosphere, 0.40 mmol) resulted, and on filtration a quantitative yield of sodium toluenesulfinate dihydrate (0.088 g, 41 mmol) was collected with ir spectrum (KBr) identical to that reported.[84] The oil obtained after solvent evaporation (0.102 g, 0.38 mmol, 95% yield) was primarily the single material, 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene (42), by nmr and tlc (trace amounts of H-shift isomers and cycloheptatriene to toluene rearrangement products are apparently the only impurities). Two successive preparative layer chromatography separations (pentane, 3 elutions) yielded 42 as the most rapidly moving, major component. Recrystallization of the solid obtained from hexane and then from methanol gave analytically pure 42 (0.025 g, 0.093 mmol, 23% yield): mp 127-128°; uv: λ_{max}(iso-octane), 348 nm

(ε 390), 341 (sh, 340), 339 (370), 332 (540), 324 (sh, 520), 297 (12,400), 285 (11,600), 276 (16,600), 254 (61,300), 247 (53,600), 222 (31,400); ir (KBr): 3060, 3030, 3010, 2850, 1600, 1490, 1450, 1430, 1255, 1145, 950, 900, 885, 770, 745, 730, 720, 710, 700, 620, 415 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 1.2-1.5 (m, 2H), 1.8-2.7 (m, 6H), 3.15-3.3 (narrow d of doublets, 2H), 3.5-3.85 (m, 2H), 4.2-4.5 (d of doublets, 2H), 6.4-6.7 (broad t, 1H); mass spectrum: m/e 268 (M^+, 100), 267 (M^+-1, 68).

Anal. Calcd. for $C_{21}H_{17}$: C, 93.99; H, 6.01. Found: C, 93.73; H, 6.11.

b) Room temperature photolysis of 5*H*-dibenzo[*a*,*c*]-cyclohepten-5-one tosylhydrazone sodium salt (41') (0.10 g, 0.25 mmol) for 50 minutes in 30 ml of benzene produced after filtration and solvent evaporation a yellow oil from which, after preparative layer chromatography (pentane, 3 elutions), 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene (42) (0.035 g, 0.13 mmol; 52% yield) was isolated. Recrystallization (hexane) gave pure 42 with physical and spectral properties identical to those of 42 formed by thermolysis of the salt (see (a) above).

c). Low temperature photolysis at -60° of 5*H*-dibenzo-[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.10 g, 0.25 mmol) in 27 ml of a 1:2 solution of benzene-tetrahydrofuran was carried out for 50 minutes at room temperature and worked up in a similar manner. 9-(2,4,6-Cycloheptatrien-1-yl)-phenanthrene (42) (3.-10. x 10^{-5} g,

1.3×10^{-4} mmol, 0.04-0.13% yield) was isolated by preparative layer chromatography (pentane, 3 elutions) and quantitatively determined by uv spectroscopy.

Low Temperature Photolysis of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone Sodium Salt (41') in Tetrahydrofuran.--5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.10 g, 0.25 mmol) was photolyzed 1 hour at -60° in 15 ml of dry tetrahydrofuran. The yellow reaction mixture was warmed to room temperature and filtered. Solvent was evaporated. An nmr spectrum of the residue indicated a low yield of chloroform soluble products, predominantly if not completely aromatic proton resonances were observed (<10% phenanthryl); tlc (cyclohexane-benzene, 2:1) showed numerous components with a good deal of streaking. Isolation and characterization of these minor compounds was not attempted.

Low Temperature Photolysis of the Sodium Salt of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone (41') in the Presence of Styrene.--5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.16 g, 0.40 mmol) was photolyzed 1 hour at -60° in 15 ml of dry tetrahydrofuran containing styrene (2.50 g, 24.0 mmol, inhibitor removed by putting through Grade I Woelm alumina). The solution was warmed to room temperature and suction filtered. The solvent was evaporated and styrene removed *in vacuo* at room temperature. Nmr and tlc of the residue were very similar to those

of the product mixture obtained from photolysis in the absence of styrene (no vinyl protons in the nmr to a limit of detection of ~2%). Attempted sublimation (4 hours, 100°, 0.15 mm of Hg) failed to transfer any material to the cold finger.

Low Temperature Photolysis of the Sodium Salt of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone (41') in the Presence of Dimethyl Fumarate.--5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.212 g, 0.538 mmol) was photolyzed 1.5 hours at -60° in 30 ml of a saturated, dry tetrahydrofuran solution of dimethyl fumarate (2.50 g, 18.0 mmol, recrystallized from chloroform-hexane). The solution was allowed to come to room temperature and suction filtered. The solvent was removed and dimethyl fumarate sublimed away at 40° (0.2 mm of Hg, overnight). The ^{1}H-nmr spectrum of the residue showed no vinyl protons to a limit of detection of ~2% and was similar to that of the reaction mixture obtained on photolysis in the absence of dimethyl fumarate; tlc, also, gave no indication of dimethyl fumarate reaction products.

Low Temperature Photolysis of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone Sodium Salt (41') in the Presence of 1,3-Cyclopentadiene.--5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.20 g, 0.50 mmol) was photolyzed 40 minutes at -60° in 20 ml dry tetrahydrofuran containing freshly prepared cyclopentadiene monomer[83]

(5 ml, 75 mmol). The reaction mixture was allowed to warm to 5°, and solvent was removed under reduced pressure. (The last trace of dicyclopentadiene was removed *in vacuo*.) The residue was taken up in cyclohexane and column chromatographed on silica gel (cyclohexane). A single component, *endo*-2,3-(*o*-biphenylenyl)-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (43) (0.094 g, 0.37 mmol, 73% yield), eluted from the column. Molecular distillation (110°, 0.2 mm of Hg) yielded a pure, colorless liquid with the following properties: uv: λ_{max}(iso-octane), 308 nm (ε 2,300), 273 (4,700), 257 (5,100), 248 (7,700), 239 (8,200), 221 (14,000); ir (film): 3060, 3030, 2970, 2930, 2860, 1600, 1490, 1445, 1330, 1245, 1045, 1020, 890, 850, 790, 745, 740, 725, 695, 675, 620 cm^{-1}; ^{1}H-nmr (CCl_4): τ 2.0-2.3 (m, 2H), 2.4-2.7 (m, 2H), 2.75-3.05 (m, 4H), 3.95 (ca. t, 2H), 6.61 (bs, H1, 1H), 6.89 (bs, H5, 1H), 7.49 (d, H3, $J_{3,4}$=2.8 Hz, 1H), 7.73 (d, H8, J_{gem}=6.8 Hz, 1H), 8.10 (d, H8, 1H), 9.39 (d of doublets, H4, $J_{3,4}$=2.8 Hz, $J_{4,5}$=2.6 Hz, 1H); mass spectrum: m/e 256 (M^+, 100), 216 (75), 192 (52).

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.50; H, 6.41.

Low Temperature Photolysis of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone Sodium Salt (41') with Subsequent Addition of 1,3-Cyclopentadiene.--a) 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.103 g, 0.260 mmol) was placed in 25 ml dry tetrahydrofuran. The

solution was cooled to -60° and photolyzed 7 minutes with rapid stirring. The light was extinguished, and 1,3-cyclopentadiene (7 ml, 100 mmol) at -78° was added within 3 seconds. The solution was allowed to warm to 5°, and solvent was partially removed under reduced pressure. The solution was filtered, and the remainder of solvent was evaporated (the last trace of dicyclopentadiene being removed under hard vacuum). The cyclopentadiene adduct 43 was isolated by preparative layer chromatography (pentane, 3 elutions) side-by-side with authentic material on the same plate. An ultraviolet spectrum in iso-octane established the presence of 43 (0.0031 g, 0.012 mmol, 4.7% yield).

b) In an identical experiment, 1,3-cyclopentadiene was added 125 seconds after photolysis ceased. An equivalent workup and quantitative determination by uv spectrophotometry indicated the formation of adduct 43 (0.0024 g, 0.0094 mmol, 3.6% yield).

Generation of Dibenzo[*a*,*c*]cycloheptatrienylidene (32) in the Presence of Furan.--a) 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.15 g, 0.38 mmol) was photolyzed 30 minutes at -60° in a 1:1 by volume solution of dry tetrahydrofuran and furan (freshly distilled from sodium hydroxide) of total volume 25 ml. The reaction mixture was allowed to come to room temperature and filtered. Solvent was removed, and the remaining yellow oil was separated by preparative layer chromatography (benzene, 2 elutions). The major product, 1,7-(*o*-biphenylenyl)-*endo*-2,5-

epoxynorcar-3-ene (44) (0.046 g, 0.18 mmol, 47% yield), was the fourth distinguishable band (just preceding a pale yellow material) on the preparative plate and quenched uv light rather poorly. Recrystallization from benzene-hexane and then from 95% ethanol gave white needles with the following properties: mp 157-158°; uv: $\lambda_{max}(CH_3CN)$, 307 nm (ε 3,400), 268 (sh, 14,300), 234 (30,600); ir (KBr): 3060, 3030, 1490, 1450, 1435, 1045, 1000, 970, 760, 745, 730, 620 575 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 1.9-2.15 (m, 2H), 2.4-3.0 (m, 7H), 3.35-3.55 (d of doublets, 1H), 4.98 (d of doublets, 2H), 6.39 (d, $J_{6,7}$=2.6 Hz, 1H), 9.60 (d, $J_{6,7}$=2.6 Hz, 1H); Table 7 lists ^{1}H-nmr ($CDCl_3$) as a function of mole ratio of Eu(fod)$_3$ added (nonaromatic protons only, 0.035 g 44 in 0.5 ml $CDCl_3$, see, also, Figure 7):

Table 7

Effect of Added Shift Reagent on ^{1}H-nmr Spectra of Adduct 44

Mole ratio Eu(fod)$_3$:44	Hz Downfield from TMS at 100.1 MHz H2	H3	H4	H5	H6	H7
0.0	506	707	652	499	40	361
0.2	1197	954	914	1187	349	1149
0.4	1739	1153	1118	1674	582	1760
0.6	2180	1322	1286	1980	744	2220

mass spectrum: m/e 258 (M^+) (low temperature required or the M^+ peak disappears and one at 380 appears).

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.27; H, 5.51.

b) Room temperature photolysis of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.143 g, 0.36 mmol) in a 1:1 by volume tetrahydrofuran-furan solution (40 ml) for 15 minutes with other conditions and workup identical to those employed in the low temperature photolysis experiment yielded adduct 44 (0.040 g, 0.15 mmol, 43% yield) as the major product. Physical and spectral properties were as reported for the material formed on low temperature photolysis.

c) Room temperature photolysis of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.117 g, 0.30 mmol) in 25 ml 1:1 by volume tetrahydrofuran-furan for 50 minutes with conditions and workup identical to those of (b) above gave 1,7-(*o*-biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (44) (0.004 g, 0.015 mmol, 5% yield) as a minor product.

d) Pyrolysis of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.10 g, 0.25 mmol) was carried out at 115° in 15 ml furan for 30 minutes. The reaction mixture was cooled and suction filtered. Furan was evaporated. Adduct 44 (0.0072 g, 0.028 mmol, 11% yield) was isolated by preparative layer chromatography (benzene, 2 elutions) as a minor product and was identical by tlc, uv, and ^{1}H-nmr to material previously obtained. There was no indication of any *exo*-epoxy isomer.

Photolysis of 1,7-(*o*-Biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (44).--1,7-(*o*-Biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (44) (0.025 g, 0.10 mmol) was photolyzed 1 hour in 30 ml dry tetrahydrofuran. Adduct 44 was completely destroyed

(<5% remaining). Three products resulted and were separated by preparative layer chromatography (benzene). Two of these components had the blue fluorescence under uv irradiation commonly associated with substituted phenanthrenes. The major product (R_f=0.2, blue fluorescence, 0.013 g) had an nmr that implies a phenanthro[*]cycloheptatrien-1-ol structure: ^{1}H-nmr ($CDCl_3$): τ 1.2-1.6 (m, 2H), 1.85-2.6 (m, 6H), 3.3 (ca. d, 1H), 3.8 (bs, 2H), 4.7 (ca. d, 1H), 6.5 (d, 1H), 7.15 (s, 1H). The other two compounds were isolated in only minor amounts: R_f=0.8, blue fluorescence, 0.003 g; R_f=0.6, 0.003 g.

Pyrolysis of 1,7-(*o*-Biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (44) in Benzene.--1,7-(*o*-Biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (1.194×10^{-3} g, 4.63×10^{-3} mmol) was dissolved in 5 ml benzene (spectrograde) and heated at 125±5° under nitrogen in a sealed tube for 2 hours. Tlc (pentane/5% benzene) showed complete destruction of starting material and formation of a single new product with R_f about twice that of starting material 44. The new product was not 9-(2,4,6-cycloheptatrien-1-yl)-phenanthrene (42) as shown by a tlc comparison with a previously characterized sample of this compound although it had a similar blue fluorescence under uv light. Nmr (microtube) suggested that this pyrolysis product was a substituted phenanthrene (τ 1.1-1.4 (m, 2H) and 2.1-2.9 (m, 6H)).

Pyrolysis of 5*H*-Dibenzo[*a*,*e*]cycloheptен-5-one Tosylhydrazone Sodium Salt (41') in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone.--5*H*-Dibenzo[*a*,*e*]cycloheptен-5-one sodium salt (41') (0.32 g, 0.80 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (1.00 g, 2.6 mmol) were dissolved in 15 ml dry tetrahydrofuran and stirred rapidly at 110±5° for 3.5 hours in a 3 oz Fisher-Porter Aerosol Compatibility Tube. The tube was cooled to room temperature, propiolic acid (1.09 g, 15.6 mmol) added, and the mixture reheated in the sealed tube at 110±5° for 80 minutes and then cooled and diluted with 50 ml toluene. Sodium carbonate was added. The mixture was stirred 4 hours and filtered. Solvent was removed, and preparative layer chromatography (cyclohexane-benzene, 2:1, 3 elutions) permitted isolation of the principal product as the only major band that moved up the plate (fastest moving band, intense blue fluorescence under uv light). The product, 10,11,12,13-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46) (0.218 g, 0.40 mmol, 50% yield), crystallized as a white powder contaminated with a trace of 9,10,11,12-tetraphenyl-11*H*-cyclohepta[*l*]phenanthrene (47) or perhaps 9,10,11,12-tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (47') [^{1}H-nmr ($CDCl_3$): τ 4.52 (bs, methine,H)]. Recrystallization from benzene-pentane gave pure 46 (0.167 g, 0.31 mmol, 38% yield) with the following properties: mp 214-215°; uv: λ_{max}(CH_3CN), 357 nm (ε 1,300), 338 (sh, 3,200), 272 (sh, 42,000), 257 (60,000); ir (KBr): 3080, 3060, 3020, 1600, 1490, 1440, 1075, 1020, 910, 755, 720, 700 cm^{-1}; ^{1}H-nmr

($CDCl_3$): τ 1.25-1.6 (m, 2H), 1.85-2.25 (m, 2H), 2.4-2.9 (m, 4H), 3.09 (bs, 20H), 5.38 (d, J=12.5 Hz, 1H), 6.08 (d, J=12.5 Hz, 1H); mass spectrum: m/e 546 (M^+, 100), 469 (17), 455 (13), 392 (26), 369 (45), 292 (14), 290 (19).

Anal. Calcd. for $C_{43}H_{30}$: C, 94.47; H, 5.53. Found: C, 94.27; H, 5.67.

Thermal Rearrangement of 10,11,12,13-Tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46).--a) 10,11,12,13-Tetraphenyl-9*H*-cyclohepta[*l*]phenanthrene (46) (0.07 g, 0.13 mmol) was dissolved in 0.5 ml tetrachloroethylene and placed in an nmr tube. Nmr spectra were taken as the temperature was gradually increased. No change in the spectrum occurred until the temperature reached 150°. Heating at 160° for 1 hour caused the doublet of doublets (τ 5.38 and 6.08, J=12.5 Hz) to lose resolution and broad humps to appear in the same region of the spectrum. On cooling the nmr spectrum showed the doublets due to 46 along with the broad singlet (τ 4.52) due to an H-shift isomer 47 or 47' and totally aromatic material. Preparative layer chromatography (cyclohexane-benzene, 2:1, 3 elutions) failed to separate the components. Recrystallization from chloroform also failed to give a pure product. The mass spectrum of the mixture had a parent ion at 546 of more than 5 times the intensity of any other fragment, and a mp 297-299° was recorded.

b) Refluxing 46 in xylene 5 hours produced a mixture with an nmr spectrum similar to that obtained after heating

in the nmr probe above. Heating in xylene at reflux for an additional 5 hours reduced the amount of 46 and 47 slightly relative to the totally aromatic material.

Low Temperature Photolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt (53') in the Presence of 1,3-Cyclopentadiene.--4,5-Benzotropone tosylhydrazone sodium salt (53') (0.256 g, 0.74 mmol) was photolyzed 75 minutes at -60° in 20 ml dry tetrahydrofuran containing 1,3-cyclopentadiene monomer[83] (7 ml, 100 mmol, transferred at -78°). The reaction mixture was allowed to warm to 5°, and solvent and cyclopentadiene were removed under reduced pressure. The residue was taken up in cyclohexane and passed through an alumina column (Grade III) to remove sodium toluenesulfinate and a very slightly soluble red material that seemed to be the major product. Solvent removal left the hydrocarbon products (0.038 g), mainly *endo*-5,6-benzotetracyclo[7.2.1.$0^{2,7}$.$0^{2,8}$]dodeca-3,5,10-triene (48) and a number of minor components that appeared (nmr) to be secondary photolysis products and naphthylcarbene addition and insertion products. Preparative layer chromatography (pentane, 3 elutions, the leading band isolated) followed by molecular distillation (90°, 0.15 mm of Hg) gave a colorless liquid (0.025 g, 0.12 mmol, 16% yield) with the following properties: ir (film): 3060, 3020, 2970, 2930, 2860, 1485, 1455, 1330, 1235, 1040, 1025, 1000, 895, 860, 840, 785, 770, 755, 740, 730, 625 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.65-2.95 (m, 4H),

3.71 (narrow AB pattern, 2H), 3.9-4.25 (m, 2H), 6.93 (bs, 1H), 7.05 (bs, 1H), 7.52 (d, $J_{7,8}$=2.8 Hz, 1H), 7.75-8.0 (m, J_{gem}=6.8 Hz, 1H), 8.18 (d, J_{gem}=6.8 Hz, 1H), 9.65 (narrow d of doublets, $J_{7,8}$=2.8 Hz, $J_{8,9}$=2.6 Hz, 1H); mass spectrum: m/e 206 (M^+, 100), 178 (54), 165 (69); exact mass 206.1091 (calcd. for $C_{16}H_{14}$, 206.1095).

Pyrolysis of *endo*-5,6-Benzotetracyclo[7.2.1.$0^{2,7}$.$0^{2,8}$]-dodeca-3,5,10-triene (48).--Attempted preparative gas chromatography of *endo*-5,6-benzotetracyclo[7.2.1.$0^{2,7}$.$0^{2,8}$]dodeca-3,5,10-triene (48) at 160° (18' x 1/4", 20% SE-30) gave a single compound with tlc (pentane) and nmr spectrum different from the initially injected sample of 48. The nmr spectrum is consistent with a structure such as 7,10-methano-11*H*-naphtho[*a*]cycloheptene: ^{1}H-nmr ($CDCl_3$): τ 2.05-3.0 (m, 6H), 3.6-3.8 (d of doublets, 1H), 4.1-4.3 (d of doublets, 1H), 6.5-6.7 (m, 1H), 6.8-7.4 (m, 3H), 7.6-8.1 (m, 3H). This material is also present as a minor product formed in the preparation of 48 and is distinguishable in the nmr spectrum of the mixture of crude hydrocarbon products. No attempt was made to purify and characterize this material.

Low Temperature Photolysis of 3,4-Benzotropone Tosylhydrazone Sodium Salt (53') in the Presence of 1,3-Butadiene.--4,5-Benzotropone tosylhydrazone sodium salt (53') (0.228 g, 0.66 mmol) in 15 ml dry tetrahydrofuran was cooled to -60° in the photolysis cell. An equal volume of 1,3-butadiene was condensed into the cell, and photolysis was

carried out for 2 hours. The reaction mixture was warmed to room temperature under a stream of nitrogen as the butadiene evaporated. The solution was further reduced in volume at 25° under reduced pressure and filtered through magnesium sulfate (anhydrous) to remove sodium toluenesulfinate and an amorphous red solid that precipitated. Preparative layer chromatography (pentane, 3 elutions) permitted the isolation of two C_{15} isomers. The leading component, 4,5-benzotricyclo[5.4.0.0^{1,6}]undeca-2,4,9-triene (49) (0.014 g, 0.072 mmol, 11% yield), was obtained after molecular distillation (70°, 0.15 mm of Hg) as a colorless liquid with the following properties: uv: λ_{max}(iso-octane), 308 nm (sh, ε 1,600), 276 (6,050), 223 (22,000); ir (film): 3020, 2890, 2830, 1485, 1455, 1435, 1220, 1115, 1055, 980, 795, 780, 765, 750, 725, 670, 645 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.6-3.0 (m, 4H), 3.84 (AB pattern, 2H), 4.35-4.55 (m, 2H), 7.47 (bs, 4H), 7.64 (d, $J_{6,7}$=4.7 Hz, 1H), 9.45-9.75 (m, 1H); mass spectrum: m/e 194 (M^+, 22), 179 (27), 141 (89), 140 (100), 124 (34); exact mass 194.108 (calcd. for $C_{15}H_{14}$, 194.1095).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.64; H, 7.28.

The trailing component was highly contaminated with impurities, but an additional preparative layer chromatography (pentane, 5 elutions) permitted isolation of 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (50) (0.003 g, 0.016 mmol, 3% yield) by judicious removal of the center portion of a

broad band of poorly separated compounds. After molecular distillation (70°, 0.15 mm of Hg) this spiro-compound 50 had the following properties: ir (film): 3060, 3020, 1630, 1490, 1440, 1155, 1040, 990, 940, 900, 810, 760, 745, 705 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.96 (s, 4H), 3.72 (d, $J_{4,5}$=11.5 Hz, 1H), 3.84 (d, $J_{8,9}$=11.5 Hz, 1H), 4.2-4.8 (m, 1H), 4.75-5.2 (m, 3H), 8.25-9.2 (m, 3H); mass spectrum: m/e 194 (M^+, 73), 179 (100), 178 (62), 165 (45), 128 (96); exact mass 194.1085 (calcd. for $C_{15}H_{14}$, 194.1095).

Low Temperature Photolysis of 1-Vinyl-6,7-benzospiro-[2.6]nona-4,6,8-triene (50).--In the small volume photolysis cell (Pyrex) employing the standard conditions for low temperature formation of aromatic carbenes from tosylhydrazone salts, 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (50) (0.002 g, 0.01 mmol) was photolyzed 1 hour at -60° in 20 ml dry tetrahydrofuran. Solvent removal followed by preparative layer chromatography (pentane/5% benzene) gave approximately 75% recovery of starting material 50 along with trace amounts of two other materials neither of which was 4,5-benzotricyclo[5.4.0.$0^{1,6}$]undeca-2,4,9-triene (49) as determined by tlc and uv. No trace of 49 could be detected by uv spectrophotometry when that portion of the preparative layer chromatography plate expected to contain this compound (chromatographed side-by-side with an authentic sample of 49 on the same plate) was extracted. The limit of detection by uv was better than 2. x 10^{-5} g (1%).

Pyrolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt (53') in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone.--4,5-Benzotropone tosylhydrazone sodium salt (53') (0.36 g, 1.05 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (1.0 g, 2.6 mmol) were dissolved in 15 ml dry tetrahydrofuran and stirred rapidly at 115±5° for 2 hours in a sealed tube under nitrogen. Solvent was removed under reduced pressure, and the reaction products dissolved in 50 ml toluene. Propiolic acid (1.0 g, 14 mmol) was added, and the solution heated at reflux 30 minutes (until the tetracyclone color lightened). The solution was cooled, and an excess of sodium carbonate added. After stirring 30 minutes, the mixture was filtered through Celite^{R} 545. Solvent was removed under reduced pressure, and the residue twice subjected to preparative layer chromatography (benzene-carbon tetrachloride-pentane, 1:1:1, 3 elutions). Three products were obtained. 7,8,9,10-Tetraphenyl-9*H*-cyclohepta[*a*]naphthalene (54) (0.046 g, 0.093 mmol, 9% yield) was the fastest moving component and had a bright blue fluorescence under uv light. It was recrystallized from benzene-pentane as a colorless solid with the following properties: mp 212-213°; uv: $\lambda_{max}(CH_3CN)$, 330 nm (sh, ε 13,000), 281 (39,500), 240 (41,000); ir (KBr): 3060, 3010, 2920, 1600, 1495, 1445, 1080, 1035, 820, 770, 700, 600, 550, 530 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 1.6-1.9 (m, 1H), 2.21 (bs, 1H), 2.3-3.3 (m, 25H), 4.57 (bs, 1H); mass spectrum: m/e 496 (M^+, 100), 419 (17), 406 (10), 342 (59); exact mass 496.2143 (calcd. for $C_{39}H_{28}$,

496.2191). The second component on the plate (0.160 g, 0.305 mmol, 29% yield) was tentatively identified as 6*a*,11*a*-dihydro-7,8,9,10-tetraphenylbenzo[*a*]naphtho[2,1-*d*]furan (56) from the following spectral properties of 56 after a recrystallization from benzene-pentane: mp 275-277°; uv: $\lambda_{max}(CH_3CN)$, 300 nm (ε 6,800), 243 (45,000); ir (KBr): 3060, 3030, 2910, 1600, 1565, 1495, 1445, 1400, 1295, 1210, 1160, 1075, 1030, 940, 915, 830, 795, 755, 700, 660, 600, 560, 545 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.5-3.0 (m, 9H), 3.20 (bs, 15H), 3.69 (d of doublets, $J_{5,6}$=9 Hz, $J_{5,6a}$=2.5 Hz, 1H), 4.24 (d, $J_{6a,11a}$=9 Hz, 1H), 4.76 (d of doublets, $J_{5,6}$=9 Hz, $J_{6,6a}$=3 Hz, 1H), 5.58 (d of triplets, $J_{6a,11a}$=9 Hz, $J_{5,6a}$=$J_{6,6a}$=2.5-3. Hz, 1H); mass spectrum: m/e 524 (M^+).

Anal. Calcd. for $C_{40}H_{28}O$: C, 91.57; H, 5.38. Found: C, 91.25; H, 5.40.

The third product with the smallest R_f value was β-naphthyltetraphenylphenol (55) (0.094 g, 0.18 mmol, 17% yield). The optimum yield of 55 may not have been obtained since workup conditions could have removed a portion of this product. The crude material became bright orange in the presence of sodium hydroxide and an nmr signal at τ 4.78 was removed by shaking with deuterium oxide. Recrystallization from ethanol-water gave pure 55 with the following properties: mp 235-237°; ir (KBr): 3530, 3050, 3020, 1600, 1500, 1440, 1400, 1290, 1270, 1200, 1135, 1105, 1070, 750, 725, 700, 600, 480 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.2-2.9 (m, 12H), 3.2 (d, 15H), 4.78 (s, 1H); mass spectrum: m/e 524 (M^+).

Anal. Calcd. for $C_{40}H_{24}O$: C, 91.57; H, 5.38. Found: C, 91.39; H, 5.42.

Thermolysis of 54, 55, and 56 each in a separate sealed tube at 115±5° in tetrahydrofuran for 2 hours failed to convert any compound to any other. All were stable to the thermolysis conditions as determined by tlc (benzene). 55 and 56 were also stable to p-toluenesulfonic acid treatment in acetonitrile at room temperature for 24 hours as determined by tlc (benzene).

Pyrolysis of Tropone Tosylhydrazone Sodium Salt in Furan.--Tropone tosylhydrazone sodium salt (0.50 g, 1.7 mmol) in 30 ml furan was heated at 120±3° for 2 hours in a sealed tube. The dark reaction mixture was cooled to room temperature and filtered. The solvent volume was reduced to a convenient size for transfer to a preparative layer chromatography plate. Chromatography (pentane-ether-benzene, 5:3:2, 2 elutions) gave *exo*-1,4-epoxy-4*aH*-benzocycloheptene (57) (0.155 g, 0.98 mmol, 58% yield) as the major product along with heptafulvalene. The R_f of 57 was about twice that of heptafulvalene. Nmr spectra of the minor components gave no indication of the *endo*-epoxy isomer. Adduct 57 solidified on vacuum transfer and had the following properties: mp 47-48.5°; uv: $\lambda_{max}(CH_3CN)$, 304 nm (ε 1,700), 201 (18,000); ir (melt): 3020, 2860, 1315, 1290, 1055, 1030, 1000, 900, 860, 850, 825, 785, 765, 725, 705, 695, 630 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 3.17 (d of doublets, $J_{1,2}$=2 Hz, $J_{2,3}$=6 Hz,

1H), 3.71 (d of doublets, $J_{2,3}$=6 Hz, $J_{3,4}$=1.7 Hz, 1H), 3.8-4.4 (m, 4H), 4.63 (bd, $J_{4,4a}$=4.5 Hz, 1H), 5.00 (bs, 1H), 5.54 (d of doublets, $J_{4a,5}$=3.5 Hz, $J_{5,6}$=9 Hz, 1H), 6.45-6.65 (m, 1H); Table 8 lists ^{1}H-nmr (CCl_4) as a function of mole ratio of Eu(fod)$_3$ added (0.060 g 57 in 0.5 ml CCl_4, see, also, Figure 10):

Table 8

Effect of Added Shift Reagent on ^{1}H-nmr Spectra of Adduct 57

Mole ratio	Hz Downfield from TMS at 100.1 MHz							
Eu(fod)$_3$:57	H1	H2	H3	H4	H4a	H5	H6,7,8	H9
0.0	487	675	619	525	337	436	590	610
0.2	1144	945	888	1150	749	661	705	775
0.4	1550	1104	1042	1557	1025	741	723	843

mass spectrum: m/e 158 (M^+, 74), 129 (100), 128 (98), 105 (61).

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.38; H, 6.43.

Generation of Phenanthrylcarbene (33) in the Presence of Furan.--a) Phenanthrene-9-carboxaldehyde tosylhydrazone sodium salt (45') (0.25 g, 0.63 mmol) was photolyzed 1.5 hours at -60° in a 1:1 by volume solution of tetrahydrofuran-furan of total volume 30 ml. The reaction mixture was allowed to come to room temperature and filtered. Solvent was removed, and the residue was inspected by ^{1}H-nmr spectroscopy. There was no indication of the formation of any 1,7-(*o*-biphenylenyl)*endo*-2,5-epoxynorcar-3-ene (44).

Preparative layer chromatography (benzene, 2 elutions) side-by-side with authentic 44 on the same plate, extraction of the portion of the plate expected to contain 44, and analysis by uv spectrophotometry failed to indicate the presence of adduct 44 to a limit of detection of better than $2. \times 10^{-4}$ g (0.1% yield).

b) Phenanthrene-9-carboxaldehyde tosylhydrazone sodium salt (45') (0.50 g, 1.26 mmol) was pyrolyzed in 20 ml neat furan (sealed tube) for 1 hour at 115±5° with rapid stirring. The reaction mixture was cooled to room temperature and filtered. Solvent was removed. No trace of adduct 44 could be detected in the ^{1}H-nmr spectrum of the residue or by tlc (benzene). The ^{1}H-nmr and tlc of the product mixture were remarkably different from those of the product mixture from pyrolysis of 5*H*-dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') under similar conditions.

c) Phenanthrene-9-carboxaldehyde tosylhydrazone sodium salt (45') (2.5 g, 6.3 mmol) was placed in a sublimer and heated at 120° overnight (10^{-2} mm of Hg). Impure phenanthryldiazomethane (0.24 g, major contaminant apparently phenanthro[9,10-*c*]pyrazole[46]) collected on the sublimer cold finger. The diazo-compound was dissolved in 20 ml of a 1:1 by volume solution of tetrahydrofuran-furan and photolyzed at room temperature for 20 minutes. Solvent was removed. No trace of adduct 44 was indicated by nmr or tlc (benzene) of the residue.

Low Temperature Photolysis of the Sodium Salt of 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one Tosylhydrazone (41') in the Presence of Diethylamine.--a) 5*H*-Dibenzo[*a*,*c*]cyclohepten-5-one tosylhydrazone sodium salt (41') (0.20 g, 0.50 mmol) and diethylamine (2.50 g, 34. mmol, distilled from LAH) were mixed in 20 ml dry tetrahydrofuran. The solution was photolyzed 45 minutes at -60°. The reaction mixture was warmed to room temperature, and the sodium toluenesulfinate dihydrate[89] (0.074 g, 0.35 mmol, 69% yield) was filtered off. Solvents were removed, and the ^{1}H-nmr spectrum of the residue gave no indication of the presence of a diethylamine addition product (no ethyl signal). Both nmr and tlc of the product mixture were similar to those of reaction mixtures from photolysis of 41' in the absence of trapping reagents or in the presence of ineffective traps such as styrene or dimethyl fumarate.

b) A similar ^{1}H-nmr spectrum resulted when a like quantity of the salt 41' was photolyzed in neat diethylamine at -30±10° with other conditions and workup similar. There was no indication of an amine adduct.

Photolysis of Phenyl Azide in the Presence of Butylamine.--a) Phenyl azide[90] (2.08 g, 17.5 mmol) was photolyzed 1 hour at room temperature in dry tetrahydrofuran containing butylamine (21. g, 290 mmol, distilled from LAH). An Hanovia preparative scale photolytic reactor (Pyrex, total volume 250 ml) was used and a nitrogen atmosphere maintained. Sol-

vent and unreacted amine were removed under reduced pressure, and the major product, 2-N-butylamino-3*H*-azepine (61b), was vacuum distilled (0.1 mm of Hg, 92-105°) from the dark residue. The product 61b (2.09 g, 12.7 mmol, 73% yield) had the anticipated[72b,91] spectral properties: ir (film): 3240, 3040, 2960, 2930, 2870, 1580, 1525, 1425, 1365, 1250, 1210, 1170, 880, 760, 740, 690 cm^{-1}; ^{1}H-nmr ($CDCl_3$): τ 2.95 (d, 1H), 3.80 (d of doublets, 1H), 4.28 (d of doublets, 1H), 4.85 (d of doublets, 1H), 5.54 (bs, 1H), 6.75 (ca. t, 2H), 7.40 (d, 2H), 8.3-8.85 (m, 4H), 8.9-9.3 (m, 3H).

b) Preparative scale photolysis of phenyl azide[90] (2.00 g, 16.8 mmol) in 250 ml dry tetrahydrofuran containing one equivalent of butylamine (1.23 g, 16.8 mmol, distilled from LAH) was carried out at room temperature under nitrogen with a 550 W Hanovia lamp in an Hanovia immersion well (Pyrex, water cooled). After photolyzing 1 hour, solvent was removed and the dark residue vacuum distilled (0.25 mm of Hg, 96-106°). 2-N-Butylamino-3*H*-azepine (61b) (1.85 g, 11.3 mmol, 67% yield) was thus obtained as a pale yellow oil with spectral properties (ir, ^{1}H-nmr) as previously reported[91] and identical with the major product 61b isolated from reaction in the presence of excess amine (see (a) above).

c) Under identical conditions to those employed in the previous experiment (see (b) above) but with furan (250 ml) rather than tetrahydrofuran as solvent, phenyl azide[90] (2.00 g, 16.8 mmol) was photolyzed in the presence of one

equivalent of butylamine (1.23 g, 16.8 mmol) for 1 hour at room temperature. After vacuum distillation (0.2 mm of Hg, 95-106°), 2-N-butylamino-3*H*-azepine (61b) (1.85 g, 11.3 mmol, 67% yield) was isolated with physical and spectral properties identical to the product obtained when tetrahydrofuran was used as solvent (see (b) above).

Photolysis of Phenyl Azide in the Presence of Furan.--Under preparative photolysis conditions at room temperature, phenyl azide[90] (0.513 g, 4.3 mmol) and furan (20 g, 290 mmol) were dissolved in approximately 250 ml dry tetrahydrofuran. Photolysis was carried out under nitrogen with rapid stirring for 5.2 hours with water cooling (550 W Hanovia lamp). Solvent was removed from the opaque red-black reaction mixture, and $CDCl_3$ added to the residue. The polymeric products were too viscous to pass through a fritted filter funnel, and the ^{1}H-nmr spectrum showed only broad humps in the aromatic region along with some unreacted phenyl azide. Tlc (benzene) streaked badly, and only the colored spot due to phenyl azide was distinguishable. The reaction mixture is apparently similar to that which results from photolysis of phenyl azide in neat tetrahydrofuran.[74]

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BIOGRAPHICAL SKETCH

Thomas Tyler Coburn was born May 8, 1943, in Montebello, California, and attended Whittier Union High School in Whittier, California. He received the B.S. degree from Harvey Mudd College in Claremont, California, June, 1965, and the M.S. degree from Yale University in January, 1967.

He worked briefly as a development chemist at Geigy Chemical Corporation in Cranston, Rhode Island. From September, 1967 until June, 1970, he was Instructor and then Assistant Professor of Chemistry at Mount Saint Mary College in Newburgh, New York.

In June, 1970, he began graduate work toward the degree of Doctor of Philosophy at the University of Florida. During graduate study he held a National Science Foundation Science Faculty Fellowship (1971-1972) and a University of Florida Graduate Council Fellowship (1972-1973).

Mr. Coburn is married to the former Susan Fones Dunn of Wethersfield, Connecticut. He is the father of Matthew Tyler and Katherine Louisa and is anticipating an additional member of the family in October, 1973.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

William M. Jones, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr.
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Robert C. Stoufer
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Arun Kumar Varma

Arun K. Varma
Associate Professor of Mathematics

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1973

Dean, Graduate School

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